This is a digital copy of a book that was preserved for generations on library shelves before it was carefully scanned by Google as part of a project to make the world's books discoverable online.

It has survived long enough for the copyright to expire and the book to enter the public domain. A public domain book is one that was never subject to copyright or whose legal copyright term has expired. Whether a book is in the public domain may vary country to country. Public domain books are our gateways to the past, representing a wealth of history, culture and knowledge that's often difficult to discover.

Marks, notations and other marginalia present in the original volume will appear in this file - a reminder of this book's long journey from the publisher to a library and finally to you.

Usage guidelines

Google is proud to partner with libraries to digitize public domain materials and make them widely accessible. Public domain books belong to the public and we are merely their custodians. Nevertheless, this work is expensive, so in order to keep providing this resource, we have taken steps to prevent abuse by commercial parties, including placing technical restrictions on automated querying.

We also ask that you:

+ *Make non-commercial use of the files* We designed Google Book Search for use by individuals, and we request that you use these files for personal, non-commercial purposes.

+ *Refrain from automated querying* Do not send automated queries of any sort to Google's system: If you are conducting research on machine translation, optical character recognition or other areas where access to a large amount of text is helpful, please contact us. We encourage the use of public domain materials for these purposes and may be able to help.

+ *Maintain attribution* The Google "watermark" you see on each file is essential for informing people about this project and helping them find additional materials through Google Book Search. Please do not remove it.

+ *Keep it legal* Whatever your use, remember that you are responsible for ensuring that what you are doing is legal. Do not assume that just because we believe a book is in the public domain for users in the United States, that the work is also in the public domain for users in other countries. Whether a book is still in copyright varies from country to country, and we can't offer guidance on whether any specific use of any specific book is allowed. Please do not assume that a book's appearance in Google Book Search means it can be used in any manner anywhere in the world. Copyright infringement liability can be quite severe.

About Google Book Search

Google's mission is to organize the world's information and to make it universally accessible and useful. Google Book Search helps readers discover the world's books while helping authors and publishers reach new audiences. You can search through the full text of this book on the web at `http://books.google.com/`

NYPL RESEARCH LIBRARIES
3 3433 06641387 7

WORKS OF

FREDERICK H. GETMAN, Ph.D.

PUBLISHED BY

JOHN WILEY & SONS, Inc.

Outlines of Theoretical Chemistry.
Second Edition, Thoroughly Revised. xv + 539 pages, 5½ × 8. 111 figures. Cloth, $3.50 net.

An Introduction to Physical Science.
vi + 257 pages, 5 × 7½. 129 figures. Cloth, $1.50 net.

Laboratory Exercises in Physical Chemistry.
Second Edition, Revised. x + 285 pages, 5 × 7½. 115 figures. Cloth, $2.00 net.

OUTLINES

OF

THEORETICAL CHEMISTRY

BY

FREDERICK H. GETMAN, Ph.D. (Johns Hopkins)

Formerly Associate Professor of Chemistry in Bryn Mawr College

SECOND EDITION, THOROUGHLY
REVISED AND ENLARGED

NEW YORK
JOHN WILEY & SONS, Inc.
London: CHAPMAN & HALL, Limited
1918

THE NEW YORK
PUBLIC LIBRARY
883031
ASTOR, LENOX AND
TILDEN FOUNDATIONS
R 1919 L

Copyright, 1913, 1918,
by
FREDERICK H. GETMAN

Stanhope Press
F. H. GILSON COMPANY
BOSTON, U.S.A.

To

E. H. G.

WHOSE TENDER SYMPATHY HAS HELPED TO
LIGHTEN THE DARKNESS OF THE DAYS
DURING WHICH THESE PAGES
WERE WRITTEN

"I look upon the common operations and practices of chymists, almost as I do on the letters of the alphabet, without whose knowledge 'tis very hard for a man to become a philosopher; and yet that knowledge is very far from being sufficient to make him one."

ROBERT BOYLE. (*The Sceptical Chymist.*)

PREFACE TO SECOND EDITION.

> "The theoretical side of physical chemistry is and will probably remain
> dominant one; it is by this peculiarity that it has exerted such a great
> fluence upon the neighboring sciences, pure and applied, and on this gro
> physical chemistry may be regarded as an excellent school of exact reason
> for all students of natural sciences." — *Arrhenius.*

The demand for a second edition of this book has not o afforded the author an opportunity to thoroughly revise t original text, but also has made it possible to include such n material as should properly find a place in an introductory te book of theoretical chemistry.

The arduousness of the task of revision and amplification been appreciably lightened by the helpful criticisms and valua suggestions which have been received from those who have u the first edition with their classes.

So numerous were the additional topics suggested that t author found himself confronted with a veritable embarrassm of riches, and not the least difficult part of his task has been t attempt to weave in as many of these suggestions as seemed to consistent with a well-balanced presentation of the entire subje

The features which distinguish this edition from the precedi edition may be briefly summarized as follows: —

1. The necessity of introducing a short chapter on the m ern conception of the atom and its structure involved further necessity of including a preliminary chapter tre ing of those radioactive phenomena upon which the grea part of our present atomic theory is based.
2. The chapter on solids has been practically rewritt the space formerly devoted to an outline of crystall

raphy being devoted in the present edition to a discussion of the absorption of heat by crystalline solids and the bearing of X-ray spectra on crystalline form.

3. The increasing importance of colloidal phenomena, not only to the chemist but also to the biologist, to the physician, and to the technologist, has made it seem desirable to rewrite the entire chapter devoted to the chemistry of colloids.
4. The Brownian movement and its bearing upon the existence of molecules has been briefly presented in a separate chapter in order to emphasize the importance of the brilliant experimental work of Perrin and others in confirming the kinetic theory.
5. The chapter treating of electromotive force has been enlarged so as to include a discussion of some of the more valuable methods which have been proposed for determining junction potentials and also to point out several useful applications of concentration cells.
6. An entirely new chapter in which an attempt has been made to present the salient facts and more important theories of photochemistry in succinct form replaces the former chapter treating of the relations between radiant and chemical energy.

Among the books to which the author has had frequent recourse in the preparation of this edition should be mentioned Rutherford's "Radioactive Substances and their Radiations," W. H. and W. L. Bragg's "X-Rays and Crystal Structure," Freundlich's "Kapillarchemie," Perrin's "Les Atomes," and Sheppard's "Photochemistry."

It is with a deep sense of gratitude that acknowledgment is made to all of those friends who have offered criticisms of the old edition and suggestions for the new. Special thanks are due to Dr. W. D. Harkins of the University of Chicago not only for suggestions but for permission to quote extensively from his papers, to Dr. J. Howard Mathews of the University of Wisconsin for numerous helpful suggestions, to Dr. Walter A. Patrick of Johns Hopkins University for criticisms of the former chapter on colloids and to Mr. John McGavack for his conscientious work in checking the answers to all of the problems. In the preparation of the indices of names and subjects the author is indebted to his wife and to Miss Mary K. Pease who have given valuable assistance in that wearisome and exacting task. To the publishers, Messrs. John Wiley and Sons, Inc., acknowledgment is made of their kindness in permitting the use of Fig. 68 taken from Chamot's "Elementary Chemical Microscopy."

FREDERICK H. GETMAN.

STAMFORD, CONN.
Aug. 7, 1918.

PREFACE.

"The last thing that we find in making a book is to know what we must put first." — Pascal.

The present book is designed to meet the requirements of classes beginning the study of theoretical or physical chemistry. A working knowledge of elementary chemistry and physics has been presupposed in the presentation of the subject, the introductory chapter being the only portion of the book in which space is devoted to a review of principles with which the student is assumed to be already fairly familiar. With the exception of a few paragraphs in which the application of the calculus is unavoidable, no use is made of the higher mathematics, so that the book should be intelligible to the student of very moderate mathematical attainments. Wherever the calculus has been employed, the student who is unfamiliar with this useful tool must accept the correctness of the results without attempting to follow the successive operations by which they are obtained.

The contributions to our knowledge in the domain of physical chemistry have increased with such rapidity within recent years, that the prospective author of a general text book finds himself confronted with the vexing problem of what to omit rather than what to include. In selecting material for this book, the author has been guided in large measure by his own experience in teaching theoretical chemistry to beginners and to advanced students. The attempt has been made to present the more difficult portions of the subject, such as the osmotic theory of solutions, the laws of equilibrium and chemical action, and the principles of electrochemistry, in a clear and logical manner. While the treatment of each topic is necessarily brief yet the effort has been made to avoid the sacrifice of clearness to brevity.

The author is fully convinced from his own experience as well as from that of his colleagues, that the complete mastery of the fundamental principles of the science is best attained through the solution of numerical examples. For this reason, typical problems have been appended to various chapters of the book.

Numerous references to original papers have been given throughout, since the importance of literary research on the part of the student is conceded by all teachers to be of prime importance.

While a brief account of radioactive phenomena might very properly be considered to lie within the scope of a general outline of theoretical chemistry, yet owing to the unparalleled growth of knowledge in this field during the last decade, the author has come to believe that a condensed statement of the main facts of radiochemistry would not be of sufficient value to justify the effort involved in its preparation.

In the original preparation of his lectures, and in their evolution into book form, the author has had frequent occasion to consult Nernst's "Theoretische Chemie," Ostwald's "Lehrbuch der allgemeinen Chemie," and Van't Hoff's "Vorlesungen ueber theoretische und physikalische Chemie." Among other books to which the author is especially indebted are the following: — Le Blanc's "Lehrbuch der Elektrochemie," Daneel's "Elektrochemie." Text books of Physical Chemistry edited by Sir William Ramsay, Bigelow's "Theoretical and Physical Chemistry." Jones' "Elements of Physical Chemistry," Reychler-Kuhn's "Physikalisch-chemische Theorieen," and Whetham's "Theory of Solution."

In the preparation of the problems the author would record his indebtedness to Abegg and Sackur's "Physikalisch-chemische Rechenaufgaben," and to Morgan's "Elements of Physical Chemistry."

It is a pleasure to acknowledge the valuable assistance rendered by Dr. Eleanor F. Bliss and Dr. Anna Jonas, who have read and revised the proof of the paragraphs treating of crystalline form. The index of titles and names has been prepared by the author's wife to whose untiring patience its completeness is due. The author would also record his thanks to those friends whose kindly criticism has helped to remove many blemishes. Finally, the author would express his appreciation of the kindness of Messrs. Adam Hilger of London, and Frits Koehler of Leipzig who have rendered great assistance by permitting the reproduction of illustrations of apparatus from their catalogs.

FREDERICK H. GETMAN.

STOCKBRIDGE, MASS.
Aug. 18, 1913.

CONTENTS

CHAP.		PAGE
	PREFACE TO SECOND EDITION	vii
	PREFACE	xi
I.	Fundamental Principles	1
II.	Classification of the Elements	20
III.	The Electron Theory	31
IV.	Radioactivity	42
V.	Atomic Structure	57
VI.	Gases	72
VII.	Liquids	104
VIII.	Solids	153
IX.	Solutions	167
X.	Dilute Solutions and Osmotic Pressure	187
XI.	Association, Dissociation and Solvation	225
XII.	Colloids	237
XIII.	Molecular Reality	279
XIV.	Thermochemistry	286
XV.	Homogeneous Equilibrium	312
XVI.	Heterogeneous Equilibrium	328
XVII.	Chemical Kinetics	359
XVIII.	Electrical Conductance	385
XIX.	Electrolytic Equilibrium and Hydrolysis	422
XX.	Electromotive Force	446
XXI.	Electrolysis and Polarization	492
XXII.	Photochemistry	504
	INDEX OF NAMES	529
	INDEX OF SUBJECTS	533

THEORETICAL CHEMISTRY.

CHAPTER I.

FUNDAMENTAL PRINCIPLES.

Theoretical Chemistry. That portion of the science of chemistry which has for its object the study of the laws controlling chemical phenomena is called theoretical or physical chemistry. The first attempt to summarize the more important facts and ideas underlying the science of chemistry was made by Dalton in 1808 in his "New System of Chemical Philosophy." The birth of the science of theoretical chemistry may be considered to be coeval with the appearance of Dalton's epoch-making book.

Theoretical chemistry is concerned with the great generalizations of chemical science and bears the same relation to chemistry that philosophy bears to the whole body of scientific truth; it aims to systematize all of the established facts of chemistry and to discover the laws governing the various phenomena of chemical action.

Law, Hypothesis and Theory. The science of chemistry is based upon experimentally established facts. When a number of facts have been collected and classified we may proceed to draw inferences as to the behavior of systems under conditions which have not been investigated. This process of reasoning by analogy we term generalization and the conclusion reached we call a *law*. It is apparent that a law is not an expression of an infallible truth, but it is rather a condensed statement of facts which have been discovered by experiment. It enables us to predict results without recourse to experiment. The fewer the number of cases in which a law has been found to be invalid, the greater becomes our confidence in it, until eventually it may come to be regarded as tantamount to a statement of fact.

Natural laws may be discovered by the correlation of experimentally determined facts, as outlined above, or by means of a speculation as to the probable cause of the phenomena in question. Such a speculation in regard to the cause of a phenomenon is called an *hypothesis*.

After an hypothesis has been subjected to the test of experiment and has been shown to apply to a large number of closely related phenomena it is termed a *theory*.

In his address to the British Association (Dundee, 1912), Professor Senier has this to say: "While the method of discovery in chemistry may be described generally, as inductive, still all the modes of inference which have come down to us from Aristotle, analogical, inductive, and deductive, are freely used. An hypothesis is framed which is then tested, directly or indirectly, by observation and experiment. All the skill, and all the resource the inquirer can command, are brought into his service; his work must be accurate; and with unqualified devotion to truth he abides by the result, and the hypothesis is established, and becomes a part of the theory of science, or is rejected or modified."

Elements and Compounds. All definite chemical substances are divided into two classes, *elements* and *compounds*.

Robert Boyle was the first to make this distinction. He defined an element as a substance which is incapable of resolution into anything simpler. The substances formed by the chemical combination of two or more elements he termed chemical compounds. This definition of an element as given by Boyle was later proposed by Lavoisier and, notwithstanding the vast accumulation of scientific knowledge since their time, the definition remains very satisfactory today.

At the present time we have a group of about eighty substances which have resisted all efforts to decompose them into simpler substances. These are the so-called chemical elements. It should be borne in mind, however, that because we have failed to resolve these substances into simpler forms of matter, we are not warranted in maintaining that such resolution may not be effected in the future.

Recent investigations of the radioactive elements have shown that they are continuously undergoing a series of transformations, one of the products of which is the inactive element helium. This behavior is contrary to the old view that transformation of one element into another is impossible. At first the attempt was made to explain it by assuming that the radioactive element was a compound of helium with another element, but since the radioactive elements possess all of the properties characteristic of elements as distinguished from compounds, and find appropriate places in the periodic table of Mendeléeff, the "compound theory" must be abandoned. Uranium and thorium, the heaviest elements known, appear to be undergoing a process of spontaneous disintegration over which we have no control. The products of this disintegration have filled the gap in the periodic table between thorium and lead with about thirty new elements, each of which is in turn undergoing transformations similar to those of the parent elements. Professor Soddy * says: "In spite of the existence at one time of a vague belief (a belief which has no foundation), that all matter may be to a certain extent radioactive, just as all matter is believed to be to a certain extent magnetic, it is recognized today that radioactivity is an exceedingly rare property of matter."

Notwithstanding these remarkable discoveries, we may still hold to the idea of an element as suggested by Boyle and Lavoisier. Professor Walker says: "The elements form a group of substances, singular not only with respect to the resistance which they offer to decomposition, but also with respect to certain regularities displayed by them and not shared by substances which are designated as compounds."

Law of the Conservation of Mass. In 1774, as the result of a series of experiments, Lavoisier established the law of the conservation of mass which may be stated as follows: *In a chemical reaction the total mass of the reacting substances is equal to the total mass of the products of the reaction.* It is sometimes stated thus: — the total mass of the universe is a constant; but this form of statement is open to the objection that we have no means of verification; it is a statement of a fact which transcends our experience.

---

* Chemistry of the Radio-Elements, p. 2.

The law of the conservation of mass has been subjected to most rigid investigation by Landolt [*] in a series of experiments extending over a period of fifteen years.

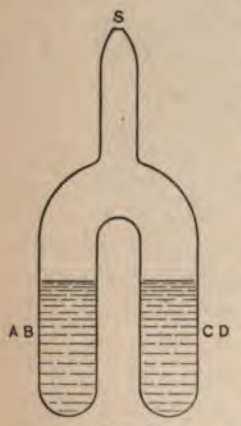


Fig. 1.

The reacting substances, AB and CD, were placed in the two arms of the inverted U-tube shown in Fig. 1 which was then sealed at S and the whole weighed upon an extremely sensitive balance. The vessel was then inverted when the following reaction took place: —

$$AB + CD \rightarrow AD + CB.$$

When the reaction was complete and sufficient time had elapsed to allow the vessel to return to its original volume (this sometimes required nearly three weeks), it was weighed again using every precaution to avoid errors and any gain or loss in weight noted. Landolt concluded from the thirty or more reactions which he studied that the gain or loss in weight was less than one ten-millionth of the total weight.[†]

Law of Definite Proportions. The enunciation of the law of the conservation of mass and the introduction of the balance into the chemical laboratory marked the beginning of a new era in the history of chemistry, — the era of quantitative chemistry. As the result of painstaking experimental work, Richter and Proust announced the law of definite proportions about the beginning of the nineteenth century. This law may be expressed thus: *A definite chemical compound always contains the same elements united in the same proportion by weight.*

Shortly after the enunciation of this law its truth was questioned by the French chemist Berthollet.[‡] From the results of a series of brilliant experiments, he became convinced that chemical reactions are largely controlled by the relative amounts of the reacting substances. As we shall see later, he really foreshadowed the work of Guldberg and Waage who were the first to correctly formulate the influence of mass on a chemical reaction. Berthollet argued that when two elements unite to form a compound, the proportion of one of the elements in the compound is conditioned solely by the amount of that element which is available. This led to the celebrated controversy between Berthollet and Proust which finally resulted in the establishment of the latter's original statement. Subsequent investigation has only strengthened our faith in the law of definite proportions.

---

[*] Zeit. phys. chem., **12**, 1 (1893); **55**, 589 (1906).

[†] An excellent summary of this important investigation will be found in Journal de Chimie physique, **6**, 625 (1908).

[‡] Essai de statique chimique (1803).

Law of Multiple Proportions. Elements are known to unite in more than one proportion by weight. Dalton analyzed the two compounds of carbon and hydrogen, methane and ethylene, and found that the ratio of the weights of carbon to hydrogen in the former was 6 : 2 while in the latter it was 6 : 1. That is, for the same weight of carbon, the weights of the hydrogen in the two compounds were in the ratio 2 : 1.

A large number of compounds were examined and similar simple ratios between the masses of the constituent elements were found. As a result of these observations, Dalton * formulated in 1808 the law of multiple proportions, as follows: *When two elements unite in more than one proportion, for a fixed mass of one element the masses of the other element bear to each other a simple ratio.* Notwithstanding the fact that Dalton was a careless experimenter the subsequent investigations of Marignac and others have established the validity of his law.

Law of Combining Proportions. Dalton pointed out that it is possible to assign to every element a definite relative weight with which it enters into chemical combination. He observed that the weights or simple multiples of the weights of the different elements which unite with a given weight of a definite element, represent the weights of the different elements which combine with each other. The weights of the elements which combine with each other are termed their *combining weights*. This comprehensive law of chemical combination may be stated as follows: *Elements combine in the ratio of their combining weights or in simple multiples of this ratio.* It will be observed that this law really includes the law of definite and the law of multiple proportions.

---

* A New System of Chemical Philosophy (1808).

If we assume the combining weight of hydrogen to be unity, the combining weights of chlorine, oxygen and sulphur will be 35.5, 8 and 16 respectively. These numbers represent the ratios in which the elements substitute each other in chemical compounds. Hydrochloric acid, for example, contains 35.5 parts by weight of chlorine to 1 part by weight of hydrogen and when oxygen is substituted for chlorine, forming water, the new compound contains 8 parts by weight of oxygen to 1 part by weight of hydrogen. Similarly, if the oxygen be substituted by sulphur, forming hydrogen sulphide, there will be found 16 parts by weight of sulphur to 1 part by weight of hydrogen. We may say, then, that 35.5 parts of chlorine, 8 parts of oxygen and 16 parts of sulphur are *equivalent.*

A *chemical equivalent* may be defined as the weight of an element which is necessary to combine with or displace 1 part by weight of hydrogen.

The Atomic Theory. In very early times two different views were entertained by opposing schools of Greek philosophers as to the mechanical constitution of matter. According to the school of Plato and Aristotle, matter was thought to be continuous within the space it appears to fill and to be capable of indefinite subdivision. According to the other school, first taught by Leucippus, and afterwards by Democritus and Epicurus, matter was considered to be made up of primordial, extremely minute particles, distinct and separable from each other but in themselves incapable of division. These ultimate particles were called *atoms* (ἡἄτομος), signifying something indivisible. While the Aristotelian doctrine held sway for many centuries yet the notion of atoms was revived at intervals. Late in the seventeenth century, Boyle seems to have looked upon chemical combination as the result of atomic association.

Guided by these early speculations as to the constitution of matter and influenced by his study of the writings of Sir Isaac Newton, Dalton seems to have formed a mental picture of the part played by atoms in the act of chemical combination. After a few carelessly performed experiments, the results of which accorded with his preconceived ideas, he formulated his atomic theory.

According to this theory matter is composed of extremely minute, indivisible particles or atoms. Atoms of the same element are all of equal weight, but atoms of different elements have weights proportional to their combining numbers. Chemical compounds are formed by the union of atoms of different kinds. This theory offers a simple, rational explanation of the laws of chemical combination.

Since a chemical compound results from the union of atoms, each of which has a definite weight, its composition must be invariable, — which is the law of definite proportions. Again, when atoms combine in more than one proportion, for a fixed weight of atoms of one kind, the weights of the other species of atoms must bear to each other a simple ratio, since the atoms are indivisible units. This is clearly the law of multiple proportions.

Finally, the law of combining weights is seen to follow as a necessary consequence of the atomic theory, since the experimentally determined combining weights bear a simple relation to the relative weights of the atoms.

At the time when Dalton proposed his atomic theory, the number of facts to be explained was comparatively small, but with the enormous growth of the science of chemistry during the past century and with the vast accumulation of data, the theory has proved capable of affording adequate representation of all of the facts, and has opened the way to many important generalizations.

While the atomic theory has played a very important part in the development of modern chemistry, and while we recognize that it helps to clarify our thinking and enables us to construct a mental image of tiny spheres uniting to form a chemical compound, yet we must not forget the fact that these atoms are purely hypothetical.

Faraday has said: "Whether matter be atomic or not, this much is certain, that granting it to be atomic, it would appear as it now does." Ostwald believes that in the not distant future the atomic theory will be abandoned and chemists will free themselves from the yoke of this hypothesis, relying solely upon the results of experiment. He says: "It seems as if the adaptability of the atomic hypothesis is near exhaustion, and it is well to realize that, according to the lesson repeatedly taught by the history of science, such an end is sooner or later inevitable."

Combining Weights and Atomic Weights. The problem of determining the relative atomic weights of the elements would at first sight appear to be a very simple matter. This might apparently be accomplished by selecting one element, say hydrogen, it being the lightest known element, as the standard; a compound of hydrogen and another element may then be analyzed and the amount of the other element in combination with one part by weight of hydrogen determined. This weight will be its atomic weight *only* when the compound contains but one atom of each element. To determine the relative atomic weight, therefore, we must know in addition to the chemical equivalent of the element, the number of atoms present in the compound. For example, the analysis of water shows it to contain 8 parts by weight of oxygen to 1 part by weight of hydrogen; the chemical equivalent of oxygen is, therefore, 8, and if water contained but one atom of hydrogen the atomic weight of oxygen would be 8. It can be shown, however, that water contains two atoms of hydrogen and one atom of oxygen, therefore, the atomic weight of oxygen must be 16. It is evident, therefore, that neither the analysis nor the synthesis of a compound is sufficient to enable us to determine the number of atoms of an element combined with one atom of hydrogen. We shall proceed to the consideration of the methods by which this problem may be solved.

Gay-Lussac's Law of Volumes. Gay-Lussac in 1808, while studying the densities of gases before and after reaction, announced the following law: *When gases combine they do so in simple ratios by volume, and the volume of the gaseous product bears a simple ratio to the volumes of the reacting gases when measured under like conditions of temperature and pressure.* Thus, one volume of hydrogen combines with one volume of chlorine to form two volumes of hydrochloric acid; one volume of oxygen combines with two volumes of hydrogen to form two volumes of water (vapor); and one volume of nitrogen combines with three volumes of hydrogen to form two volumes of ammonia.

In a previous investigation, Gay-Lussac had shown that all gases behave identically when subjected to changes of temperature and pressure. This fact, taken together with the simple volumetric relation just enunciated and the atomic theory, suggested a possible relation between the number of ultimate particles in equal volumes of different gases.

Berzelius attempted to show that under corresponding conditions of temperature and pressure, equal volumes of different gases contain the same number of atoms, but he was compelled to abandon the assumption as untenable.

Avogadro's Hypothesis. It remained for the Italian physicist, Avogadro,* in 1811, to point out the distinction between atoms and molecules, terms which had been used almost synonymously up to his time. He defined the *atom* as the smallest particle which can enter into chemical combination, whereas the *molecule* is the smallest portion of matter which can exist in a free state. He then formulated the following hypothesis:† *Under the same conditions of temperature and pressure, equal volumes of all gases contain the same number of molecules.* This hypothesis has been subjected to such rigid experimental and mathematical tests that its validity cannot be questioned.

Avogadro's Hypothesis and Molecular Weights. According to Gay-Lussac when hydrogen and chlorine combine to form hydrochloric acid, one volume of hydrogen unites with one volume of chlorine yielding two volumes of hydrochloric acid.

According to the hypothesis of Avogadro, the number of molecules of hydrochloric acid is double the number of molecules of hydrogen or of chlorine, and, consequently, each molecule of the reacting gases must contain at least two atoms. If we take hydrogen as the unit of our system of atomic weights, its molecular weight must be 2. It is convenient to express molecular and atomic weights in terms of the same unit, for then the molecular weight of a substance will be simply the sum of the weights of the atoms contained in the molecule. The determination of the approximate molecular weight of a substance, therefore, resolves itself into ascertaining the mass of its vapor in grams which, under the same conditions of temperature and pressure, will occupy the same volume as 2 grams of hydrogen.

---

* Jour. de Phys., 73, 58 (1811).

† Ampere advanced nearly the same hypothesis in 1814.

This weight is called the *gram-molecular weight* or the *molar weight* of the substance, while the corresponding volume is known as the *gram-molecular* or *molar volume*. It is nearly the same for all gases and at 0° and 760 mm. it may be taken equal to 22.4 liters. The molecular weights obtained from vapor density measurements are approximate only, because of the failure of most gases and vapors to obey the simple gas laws, a condition essential to the strict applicability of Avogadro's hypothesis.

Atomic Weights from Molecular Weights. While vapor density determinations as ordinarily carried out do not give exact molecular weights, it is an easy matter to arrive at the true values when we take into consideration the results of chemical analysis. It is apparent that the true molecular weight must be the sum of the weights of the constituent elements, these weights being exact multiples or submultiples of their combining proportions, which proportions have been determined by analysis alone. We select, as the true molecular weight, the value which is nearest to the approximate molecular weight calculated from the vapor density of the substance. For example, the molecular weight of ammonia, as computed from its vapor density, is 17.5 or, in other words, 17.5 grams of ammonia occupy the same volume as 2 grams of hydrogen, measured under the same conditions of temperature and pressure. The analysis of ammonia shows us that for every gram of hydrogen, there are present 4.67 grams of nitrogen. Hence the true molecular weight must contain a multiple of 1 gram of hydrogen and the same multiple of 4.67 grams of nitrogen. The problem is, to find what integral value must be assigned to x in the expression, $x\,(1 + 4.67)$, in order that it may give the closest approximation to 17.5. Clearly if $x = 3$ the value of the expression becomes 17, and this we take to be the true molecular weight. This gives 3 × 4.67 = 14 as the probable atomic weight of nitrogen. To decide whether the atomic weight of nitrogen is a multiple or a submultiple of 14, we must determine the molecular weights of a large number of gaseous or vaporizable compounds of nitrogen and select as the atomic weight the smallest quantity of the element which is present in any one of them.

The following table gives a list of seven gaseous compounds of nitrogen together with their gram-molecular weights, and the number of grams of the element in the gram-molecule.

Compound.	Gram-mol. Wt.	Grams Nitrogen.
Ammonia	17	14
Nitric oxide	30	14
Nitrogen peroxide	46	14
Methyl nitrate	77	14
Cyanogen chloride	61.5	14
Nitrous oxide	44	28
Cyanogen	52	28

It will be observed that the least weight of nitrogen entering into a gram-molecular weight of any of these compounds is 14 grams, and, therefore, we accept this value as the atomic weight of the element, although there is still a very slight chance that in some other compound of nitrogen a smaller weight of the element may be found. We shall proceed to point out that there are methods by which the probable values of the atomic weights may be checked.

Specific Heat and Atomic Weight. In 1819 the French chemists, Dulong and Petit,* pointed out a very simple relation between the specific heats of the elements in the solid state and their atomic weights. This relation, known as the law of Dulong and Petit, is as follows: *The product of the specific heat and the atomic weight of the solid elements is constant.* The value of this constant, called the *atomic heat,* is approximately 6.4. A little reflection will show that an alternative statement of this law is that *the*

---

* Ann. Chim. Phys., **10**, 395 (1819).

atoms of the elements in the solid state have the same thermal capacity. The specific heats, atomic weights and atomic heats of several elements are given in the subjoined table.

Element.	At. Wt.	Sp. Ht.	At. Ht.
Lithium	7	0.940	6.6
Glucinum	9	0.410	3.7
Boron (amorphous)	11	0.250	2.8
Carbon (diamond)	12	0.140	1.7
Sodium	23	0.290	6.7
Silicon (crystalline)	28	0.160	4.5
Potassium	39	0.166	6.5
Calcium	40	0.170	6.8
Iron	56	0.112	6.3
Copper	63	0.093	5.9
Zinc	65	0.093	6.1
Silver	108	0.056	6.0
Tin	119	0.054	6.5
Gold	197	0.032	6.3
Mercury	200	0.032	6.4

It is truly remarkable that elements differing as greatly as lithium and mercury differ, not only in atomic weight but in other properties as well, should have identical atomic heats. It will be observed that the atomic heats of boron, silicon, carbon and glucinum are too low. This departure from the law of Dulong and Petit is more apparent than real, for in the statement of the law there is no specification as to the temperature at which the specific heat should be determined. The specific heats of all solids vary with the temperature, this variation being greater in the case of some elements than in that of others. It has been shown that the specific heats of the above four elements increase rapidly with rise of temperature and approach limiting values. As these values are approached the product of specific heat and atomic weight approximates more and more closely to the mean value of the constant, 6.4.

The following table gives the values obtained by Weber * for carbon and silicon.

---

* Pogg. Ann., 154, 367 (1875).

CARBON (DIAMOND).

Temperature, degrees.	Sp. Ht.	At. Ht.
−50	0.0635	0.76
+10	0.1128	1.35
85	0.1765	2.12
206	0.2733	3.28
607	0.4408	5.30
806	0.4489	5.40
985	0.4589	5.50

CARBON (GRAPHITE).

Temperature, degrees.	Sp. Ht.	At. Ht.
−50	0.1138	1.37
+10	0.1604	1.93
61	0.1990	2.39
202	0.2966	3.56
642	0.4454	5.35
822	0.4539	5.45
978	0.4670	5.50

SILICON.

Temperature, degrees.	Sp. Ht.	At. Ht.
−40	0.136	3.81
+57	0.183	5.13
129	0.196	5.50
232	0.203	5.63

It is evident that this empirical relation can be used to deterine the approximate atomic weight of an element when its ecific heat is known, thus

$$\text{atomic weight} = \frac{6.4}{\text{specific heat}}.$$

he law of Dulong and Petit has been of great service in fixing d checking atomic weights.

About twenty years after the law of Dulong and Petit was rmulated, Neumann* showed that a similar relation holds for compounds of the same general chemical character. Neumann's law may be stated thus: *Similarly constituted compounds in the solid state have the same molecular heat.* Subsequently Kopp[*] pointed out that *the thermal capacity of the atoms is not appreciably altered when they enter into chemical combination*, or in other words, the molecular heat of solid compounds is an additive property, being made up of the atomic heats of the constituent elements.

---

* Pogg. Ann., 23, 1 (1831).

For example, the specific heat of $PbBr_2$ is 0.054 and its molecular weight is 366.8, therefore, the molecular heat is $0.054 \times 366.8 = 19.9$. Since there are three atoms in the molecule, $19.9 \div 3 = 6.6$ is their average atomic heat, a value in excellent agreement with the constant in the law of Dulong and Petit. Neumann's law may be used to estimate the atomic heats of elements which cannot be readily investigated in the solid state. The following table gives a list of atomic heats of elements in the solid state derived by means of Neumann's law.

Element.	At. Ht.	Element.	At. Ht.
Hydrogen	2.3	Carbon	1.8
Oxygen	4.0	Silicon	4.0
Fluorine	5.0	Phosphorus	5.4
Nitrogen	5.5	Sulphur	5.4

Isomorphism. From a study of the corresponding salts of phosphoric and arsenic acids, Mitscherlich[†] observed that they crystallize with the same number of molecules of water and are nearly identical in crystalline form, it being possible to obtain *mixed crystals* from solutions containing both salts. This suggested to Mitscherlich a line of investigation which resulted, in 1820, in the establishment of the law of isomorphism which bears his name.

This law may be stated as follows: *An equal number of atoms combined in the same manner yield the same crystal form, which is independent of the chemical nature of the atoms and dependent upon their number and position.* Thus, when one element replaces another in a compound without changing its crystalline form, Mitscherlich assumed that one element has displaced the other, atom for atom. For example, having two isomorphous substances, such as $BaCl_2.2\ H_2O$ and $BaBr_2.2\ H_2O$, we assume that the bromine in the second compound has replaced the chlorine in the first and, if the atomic weights of all of the elements in the first compound are known, then it is evident that the atomic weight of the bromine in the second compound can be easily calculated. This method was largely used by Berzelius in fixing atomic weights and in checking the values obtained by the volumetric method. It should be remembered that the converse of the law of isomorphism does not hold, since elements may replace each other, atom for atom, without preserving the same form of crystallization. Many exceptions to the law have been pointed out. For example, Mitscherlich himself showed that Na_2SO_4 and $BaMn_2O_8$ are isomorphous and yet the two molecules do not contain the same number of atoms. Furthermore, careful measurements of the interfacial angles of crystals have revealed the fact that substances which have been regarded as isomorphous are only approximately so, thus the interfacial angles of the apparently isomorphous crystalline salts given in the following table differ appreciably.

---

[*] Lieb. Ann. (1864), Suppl., 3, 5.

[†] Ann. Chim. Phys. (2), 14, 172 (1820).

Salt.	Interfacial Angle.
$MgSO_4.7\ H_2O$	89° 26′
$ZnSO_4.7\ H_2O$	88° 53′
$NiSO_4.7\ H_2O$	88° 56′

Ostwald has suggested that the term *homeomorphous* be applied to designate substances which have nearly identical form. At best the principle of isomorphism is only an approximation and should be employed with caution.

Valence. During the latter half of the nineteenth century the usefulness of the atomic theory was greatly enhanced by the introduction of certain assumptions concerning the combining power of the atoms. These assumptions, constituting the so-called doctrine of *valence*, were forced upon chemists in order that a satisfactory explanation might be offered of the phenomenon of isomerism. A consideration of the following formulas, — HCl, H_2O, NH_3, CH_4, — shows that the power to combine with hydrogen increases regularly from chlorine, which combines with hydrogen, atom for atom, to carbon, one atom of which is capable of combining with four atoms of hydrogen. Either hydrogen or chlorine, each of which is capable of combining with but one atom of the other, may be taken as an example of the simplest kind of atom. Any element like hydrogen or chlorine is called a *univalent* element, whereas elements similar to oxygen, nitrogen and carbon, which are capable of combining with two, three or four atoms of hydrogen, are called *bivalent*, *trivalent* and *quadrivalent* elements respectively. Most elements belong to one or the other of these four classes, although *quinquivalent*, *sexivalent* and *septivalent* elements are known. The familiar bonds or linkages of structural formulas are graphic representations of the valence of the atoms constituting the molecule. This useful conception of valence has made possible the prediction of the properties of many compounds before they have been discovered in nature or in the laboratory.

Atomic Weights. Among the first to recognize the importance of Dalton's atomic theory was the Swedish chemist, Berzelius. He foresaw the importance for chemists of a table of exact atomic weights and in 1810 he undertook the task of determining the combining weights of most of the known elements. For nearly six years he was engaged in determining the exact composition of a large number of compounds and calculating the combining weights of their constituent elements, thus compiling the first table of atomic weights.

Numerous investigators since Berzelius have been engaged in this important work, among whom should be mentioned Stas, Marignac, Morley and Richards. On two occasions special stimulus was given to such investigations. The first occasion was in 1815 when Prout suggested that the atomic weights of the elements are exact multiples of the atomic weight of hydrogen. The values obtained by Berzelius were incompatible with the hypothesis of Prout, although the atomic weights of several of the elements differed but little from integral values. To test the accuracy of this hypothesis, Stas undertook the determination of the atomic weights of several elements with a degree of accuracy such that his maximum experimental error was less than the difference between the atomic weight found and the nearest whole number. This important series of investigations disproved Prout's hypothesis as originally stated. The second occasion when the investigation of atomic weights received a special impulse was in 1869 when Mendeléeff brought forward the periodic classification of the elements. When the elements were arranged in the order of their atomic weights, several of them were found to fall in groups with which their chemical and physical properties did not correspond, and Mendeléeff asserted that in these cases the commonly accepted atomic weights, were erroneous. This led to the careful redetermination of the atomic weights which Mendeléeff had asserted to be faulty, and in most cases his predictions were confirmed.

In connection with the precise determination of atomic weights, the work of Cannizzaro in the latter part of the nineteenth century should be mentioned. He emphasized the importance of Avogadro's law as the basis of atomic weight determinations, and drew a sharp distinction between atomic and molecular weights, thus bringing order out of confusion and rendering possible the present system of atomic weights. In recent times, the most noteworthy investigations in this field are those of Morley on the combining ratio of hydrogen and oxygen, and the determination by T. W. Richards and his co-workers of the atomic weights of a large number of elements.

International Atomic Weights. Dalton selected hydrogen, the lightest known element, as the unit of his system of combining weights of the elements, but Berzelius pointed out that this was an unwise choice since but relatively few of the elements form stable compounds with hydrogen. He proposed, therefore, that oxygen should be taken as the standard, assigning to it the arbitrary value 100. This proposal of Berzelius, to substitute oxygen for hydrogen as the unit of atomic weights, did not receive serious consideration until quite recently when the International Committee on Atomic Weights took the matter up and, after careful deliberation, decided in favor of the oxygen standard. The

1917.
INTERNATIONAL ATOMIC WEIGHTS.

		O = 16			O = 16
Aluminium	Al	27.10	Molybdenum	Mo	96.00
Antimony	Sb	120.20	Neodymium	Nd	144.30
Argon	A	39.88	Neon	Ne	20.20
Arsenic	As	74.96	Nickel	Ni	58.68
Barium	Ba	137.37	Niton (radium emanation)	Nt	222.40
Bismuth	Bi	208.00	Nitrogen	N	14.01
Boron	B	11.00	Osmium	Os	190.90
Bromine	Br	79.92	Oxygen	O	16.00
Cadmium	Cd	112.40	Palladium	Pd	106.70
Cæsium	Cs	132.81	Phosphorus	P	31.04
Calcium	Ca	40.07	Platinum	Pt	195.20
Carbon	C	12.005	Potassium	K	39.10
Cerium	Ce	140.25	Praseodymium	Pr	140.90
Chlorine	Cl	35.46	Radium	Ra	226.00
Chromium	Cr	52.00	Rhodium	Rh	102.90
Cobalt	Co	58.97	Rubidium	Rb	85.45
Columbium	Cb	93.10	Ruthenium	Ru	101.70
Copper	Cu	63.57	Samarium	Sa	150.40
Dysprosium	Dy	162.50	Scandium	Sc	44.10
Erbium	Er	167.70	Selenium	Se	79.20
Europium	Eu	152.00	Silicon	Si	28.30
Fluorine	F	19.00	Silver	Ag	107.88
Gadolinium	Gd	157.30	Sodium	Na	23.00
Gallium	Ga	69.90	Strontium	Sr	87.63
Germanium	Ge	72.50	Sulphur	S	32.06
Glucinum	Gl	9.10	Tantalum	Ta	181.50
Gold	Au	197.20	Tellurium	Te	127.50
Helium	He	4.00	Terbium	Tb	159.20
Holmium	Ho	163.50	Thallium	Tl	204.00
Hydrogen	H	1.008	Thorium	Th	232.40
Indium	In	114.80	Thulium	Tm	168.50
Iodine	I	126.92	Tin	Sn	118.70
Iridium	Ir	193.10	Titanium	Ti	48.10
Iron	Fe	55.84	Tungsten	W	184.00
Krypton	Kr	82.92	Uranium	U	238.20
Lanthanum	La	139.00	Vanadium	V	51.00
Lead	Pb	207.20	Xenon	Xe	130.20
Lithium	Li	6.94	Ytterbium (Neoytterbium)	Yb	173.50
Lutecium	Lu	175.00	Yttrium	Yt	88.70
Magnesium	Mg	24.32	Zinc	Zn	65.37
Manganese	Mn	54.93	Zirconium	Zr	90.60
Mercury	Hg	200.60			

atomic weight of oxygen is taken as 16, and the unit to which all atomic weights are referred is one-sixteenth of this weight. The atomic weight of hydrogen on this basis is 1.008. Aside from the fact that most of the elements form compounds with oxygen which are suitable for analysis, the atomic weights of more of the elements approximate to integral values when oxygen instead of hydrogen is used as the standard.

The table on page 18 gives the values of the atomic weights as published by the International Committee on Atomic Weights for 1917.

CHAPTER II.

CLASSIFICATION OF THE ELEMENTS.

Early Attempts at Classification. Many attempts were made to classify the elements according to various properties, such as their acidic or basic characteristics or their valence. In all of these systems the same elements frequently found a place in more than one group, and elements bearing little resemblance to each other were classed together. The early attempts at classification based upon the atomic weights of the elements were not successful owing to the uncertainty as to the exact numerical values of these constants.

Prout's Hypothesis. In 1815, W. Prout, an English physician, observed that the atomic weights of the elements, as then given, did not differ greatly from whole numbers when hydrogen was taken as the standard. Hence he advanced the hypothesis that *the different elements are polymers of hydrogen.* As has already been pointed out this hypothesis led Stas to undertake his refined determinations of the atomic weights of silver, lithium, sodium, potassium, sulphur, lead, nitrogen and the halogens. As a result of his investigations he says: "I have arrived at the absolute conviction, the complete certainty, so far as is possible for a human being to attain to certainty in such matter, that the law of Prout is nothing but an illusion, a mere speculation definitely contradicted by experience." Notwithstanding the fact that Prout's hypothesis as originally stated was thus disproved by Stas, it still survived in a modified form given to it by J. B. Dumas, who suggested that one-half of the atomic weight of hydrogen should be taken as the fundamental unit. When Stas showed that his experiments excluded this possibility, Dumas suggested that the fundamental unit be taken as one-quarter of the atomic weight of hydrogen. Having begun to divide and subdivide, there was no limit to the process, and the hypothesis fell into disfavor, although the belief in a primal element, something akin to the protyle (πρώτη ὕλη) of the ancient philosophers, has survived and in modern times has reappeared in the electron theory.

Döbereiner's Triads. About 1817 J. W. Döbereiner* observed that groups of three elements could be selected from the list of the elements, all of which are chemically similar, and having atomic weights such that the atomic weight of the middle member is the arithmetical mean of the first and third members of the group. These groups of three elements he termed triads. In the following table a few of these triads are given.

Element.	At. Wt.	Mean atomic weight of triads.
Lithium	6.94	23.02
Sodium	23.00	
Potassium	39.10	
Calcium	40.07	88.72
Strontium	87.63	
Barium	137.37	
Chlorine	35.46	80.69
Bromine	79.92	
Iodine	126.92	
Sulphur	32.07	78.78
Selenium	79.2	
Tellurium	127.5	
Phosphorus	31.04	75.62
Arsenic	74.96	
Antimony	120.2	

This simple relation, first pointed out by Döbereiner, is clearly a foreshadowing of the periodic law.

The Helix of de Chancourtois. The idea of arranging the elements in the order of their atomic weights with a view to emphasizing the relationship of their chemical and physical properties, seems to have first suggested itself to M. A. E. B. de Chancourtois † in the year 1862. On a right-circular cylinder he traced what he termed a "telluric helix" at a constant angle of 45° to the axis. On this curve he laid off lengths corresponding to the atomic weights of the elements, taking as a unit of measure a length equal to one-sixteenth of a complete revolution of the cylinder. He then called attention to the fact that elements with analogous properties fall on vertical lines parallel to the generatrix. Being a mathematician and a geologist he did not express himself in such terms as would attract the attention of chemists and consequently his work remained unnoticed until recent times.

---

* Pogg. Ann., 15, 301 (1825).

† Vis Tellurique, Classement naturel des Corps Simples.

The Law of Octaves. In 1864 J. A. R. Newlands[*] pointed out that if the elements are arranged in the order of their atomic weights, the eighth element has properties very similar to the first; the ninth to the second; the tenth to the third; and so on, or to employ Newlands' own words: "*The eighth element starting from a given one is a kind of repetition of the first, like the eighth note of an octave in music.*" This peculiar relationship, termed by Newlands the *law of octaves,* is brought out in the following table.

H	Li	Gl	B	C	N	O
F	Na	Mg	Al	Si	P	S
Cl	K	Ca	Cr	Ti	Mn	Fe

Notwithstanding the fact that its author was ridiculed and his paper returned to him as unworthy of publication in the proceedings of the Chemical Society, this generalization must be regarded as the immediate forerunner of the periodic law.

The Periodic Law. Quite independently of each other and apparently in ignorance of the work of Newlands and de Chancourtois, Mendeléeff[†] in Russia and Lothar Meyer in Germany, gained a far deeper insight into the relations existing between the properties of the elements and their atomic weights. In 1869, Mendeléeff wrote: — "When I arranged the elements according to the magnitude of their atomic weights, beginning with the smallest, it became evident that there exists a kind of periodicity in their properties. I designate by the name 'periodic law' the mutual relations between the properties of the elements and their atomic weights; these relations are applicable to all the elements and have the nature of a periodic function." This important generalization may be briefly stated thus: *The properties of the elements are periodic functions of their atomic weights.*

---

[*] Chem. News, **10,** 94 (1864), Ibid., **12,** 83 (1865).

[†] Lieb. Ann. Suppl., **8,** 133 (1874).

The original table of Mendeléeff has been amended and modified as new data has accumulated and new elements have been discovered. The accompanying table, though containing several new elements and an entirely new group, is essentially the same as that of Mendeléeff. It consists of nine vertical columns, called *groups,* and twelve horizontal rows termed *series* or *periods.* The second and third periods contain eight elements each, and are known as *short periods,* while in the fourth series, starting with argon, it is necessary to pass over eighteen elements before another element, krypton, is encountered which bears a close resemblance to argon: such a series of nineteen elements is called a *long period.* The entire table is composed of two short and five long periods, the last one being incomplete. The positions of the elements are largely determined by their chemical similarity to those in the same group, the hyphens indicating the positions of undiscovered elements. The elements in Group VIII, presented difficulties when Mendeléeff attempted to place them according to their atomic weights and so he was obliged to group them by themselves. This group has wittily been designated as "the hospital for incurables." An examination of the table shows that the valence of the elements toward oxygen progresses regularly from Group O, containing elements which exhibit no combining power, up to Group VIII, where it attains a maximum value of eight in the case of osmium. The valence toward hydrogen on the other hand increases regularly from Group VII to Group IV in which the elements are quadrivalent.

THE PERIODIC SERIES OF THE ELEMENTS.

	Series.	Group O.	Group I, R_2O.	Group II, RO.	Group III, R_2O_3.	Group IV, RH_4, RO_2.	Group V, RH_3, R_2O_5.	Group VI, RH_2, RO_3.	Group VII, RH, R_2O_7.	Group VIII, RO_4.
	1	H 1.008	....	....	....	....	....	....	....	
Short period.	2	He 3.99	Li 6.94	Gl 9.1	B 11.0	C 12.00	N 14.01	O 16.00	F 19.0	
Short period.	3	Ne 20.2	Na 23.00	Mg 24.32	Al 27.1	Si 28.3	P 31.04	S 32.07	Cl 35.46	
Long period.	4	A 39.88	K 39.1	Ca 40.07	Sc 44.1	Ti 48.1	V 51.0	Cr 52.0	Mn 54.93	Fe 55.84; Co 58.97; Ni 58.68
	5	....	63.57 Cu	65.37 Zn	69.9 Ga	72.5 Ge	74.96 As	79.2 Se	79.92 Br	
Long period.	6	Kr 82.92	Rb 85.45	Sr 87.63	Yt 89.0	Zr 90.6	Nb 93.5	Mo 96	....	Ru 101.7; Rh 102.9; Pd 106.7
	7	....	107.88 Ag	112.40 Cd	114.8 In	119.0 Sn	120.2 Sb	127.5 Te	126.92 I	
Long period.	8	Xe 130.2	Cs 132.81	Ba 137.37	La 139.0	Ce 140.25	....	....	....	
	9	....	....	....	....	....	....	....	....	
Long period.	10	....	....	....	....	....	Ta 181.0	W 184.0	....	Os 190.9; Ir 193.1; Pt 195.2
	11	....	197.2 Au	200.6 Hg	204.0 Tl	207.1 Pb	208.0 Bi	....	....	
? Long period.	12	Nt 222.5	....	Ra 226.4	....	Th 232.4	....	U 238.5	....	

The formulas of the typical oxides and hydrides of the elements in the several groups are indicated at the top of each vertical column in the table, where R denotes any element in the group. The valence of elements in the long periods are apt to be variable. The elements in the second series are frequently called *bridge elements*, since they bear a closer relation to the elements in the next adjacent group than they do to any other members of the same group in succeeding series. The members of the third series are styled *typical elements*, because they exhibit the general properties and characteristics of the group. Each group is divided into subgroups, the elements on the right and left sides of a column forming families, the members of which are more closely related than are all of the elements included within the group. In other words we detect a kind of periodicity within each group.

In any given series the element with lowest atomic weight possesses the strongest basic character. Thus we find the strongly basic, alkali metals on the left side of the table, while on the right side are the acidic elements such as the halogens and sulphur. In fact, the strictly non-metallic elements are confined to the upper right-hand corner of the table.

Similarly, as we pass from the top to the bottom of the table, we observe a progressive change in the base-forming tendency of the elements; *i.e.*, as the atomic weight increases, the metallic character of the elements in each group becomes more pronounced.

Periodicity of Physical Properties. Lothar Meyer, as has been pointed out, discovered the periodic relations of the elements at about the same time as Mendeléeff. His table differed but slightly from that already given. The most important part of Meyer's * work, however, was in pointing out that various *physical* properties of the elements are periodic functions of their atomic weights. We know today that such properties as specific gravity, atomic volume, melting point, hardness, ductility, compressibility, thermal conductivity, coefficient of expansion, specific refraction, and electrical conductivity are all periodic. When the numerical values of these properties are plotted as ordinates against their atomic weights as abscissæ, we obtain wave-like curves similar to those shown in Fig. 2. The specific heats of the elements are an exception to the general rule. According to the law of Dulong and Petit, the product of specific heat and atomic weight is a constant, and consequently the graphic representation of this relation must be an equilateral hyperbola.

---

* Die Modernen Theorien der Chemie.

Applications of the Periodic Law. Mendeléeff pointed out the four following ways in which the periodic law could be employed: —(1) The classification of the elements; (2) The estimation of the atomic weights of elements; (3) The prediction of the properties of undiscovered elements; and (4) The correction of atomic weights.

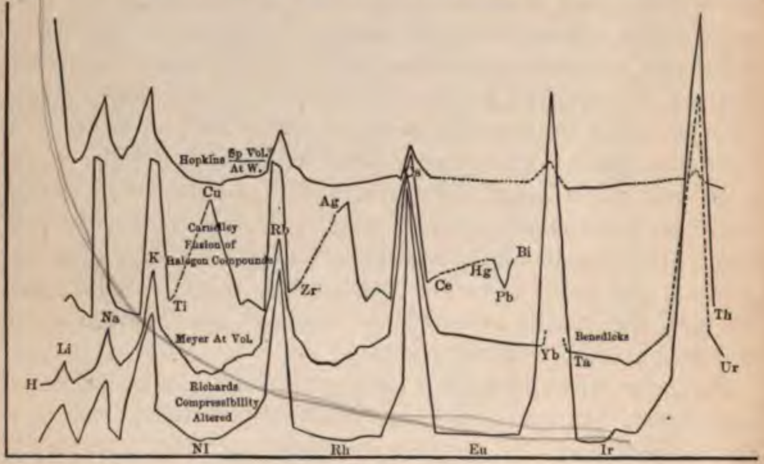


Fig. 2.

1. *Classification of Elements.* The use of the periodic law in this direction has already been indicated. It is without doubt the best system of classification known and is to be ranked among the great generalizations of the science of chemistry.

2. *Estimation of Atomic Weights.* Because of experimental difficulties it is not always possible to fix the atomic weight of an element by determinations of the vapor densities of some of its compounds, or by a determination of its specific heat. In such cases the periodic law has proved of great value. An historic

example is that of indium, the equivalent weight of which was found by Winkler to be 37.8. The atomic weight of the element was thought to be twice the equivalent weight or 75.6. If this were the correct value it would find a place in the periodic table between arsenic and selenium. Clearly there is no vacancy in the table at this point and furthermore its properties are not allied to those of arsenic or selenium. Mendeléeff proposed to assign to it an atomic weight three times its equivalent weight or 113.4, when it would fall between cadmium and tin in the table. This would bring it in the same group with aluminium, the typical element of the group, to which it bears a close resemblance. This suggestion of Mendeléeff's was confirmed by a subsequent determination of the specific heat of indium.

3. *Prediction of Properties of Undiscovered Elements.* At the time when Mendeléeff published his first table there were many more vacant spaces than exist in the present periodic table. He ventured to predict the properties of many of these unknown elements by means of the average properties of the two neighboring elements in the same series, and the two neighboring elements in the same subgroup. These four elements he termed *atomic analogues.* The undiscovered elements Mendeléeff designated by prefixing the Sanskrit numerals, eka (one), dwi (two), tri (three), and so on, to the names of the next lower elements of the subgroup. When the first periodic table was published there were two vacancies in Group III, the missing elements being called by Mendeléeff eka-aluminium and eka-boron, while in Group IV there was a vacancy below titanium, the missing element being called eka-silicon. The subsequent discovery of gallium, scandium and germanium, with properties nearly identical with those predicted for the above hypothetical elements, served to strengthen the faith of chemists in the periodic law. The following table illustrates the accuracy of Mendeléeff's prognostications: in it is given a comparison of a few of the properties of the hypothetical element, eka-silicon, as predicted by Mendeléeff in 1871, and the corresponding observed properties of germanium, discovered by Winkler fifteen years later.

Eka-silicon, Es.	Germanium, Ge.
Atomic weight, 72.	Atomic weight, 72.3.
Specific gravity, 5.5.	Specific gravity, 5.47.
Atomic volume, 13.	Atomic volume, 13.2.
Metal dirty gray, and on ignition yields a white oxide, EsO_2.	Metal grayish-white, and on ignition yields a white oxide, GeO_2.
Element decomposes steam with difficulty.	Element does not decompose water.
Acids have slight action, alkalies no pronounced action.	Metal not attacked by HCl, but acted upon by aqua regia. Solutions of KOH have no action. Oxidized by fused KOH.
Action of Na on EsO_2 or on EsK_2F_6 gives metal.	Ge obtained by reduction of GeO_2 with C, or of GeK_2F_6 with Na.
The oxide EsO_2 refractory.	The oxide GeO_2 refractory.
Specific gravity of EsO_2, 4.7.	Specific gravity of GeO_2, 4.703.
Basic properties of EsO_2 less marked than TiO_2 and SnO_2, but greater than SiO_2.	Basic properties of GeO_2 feeble.
Forms hydroxide soluble in acids, and the solutions readily decompose forming a metahydrate.	Acids do not ppt. the hydroxide from dil. alkaline solutions, but from conc. solutions, acids ppt. GeO or a metahydrate.
$EsCl_4$ a liquid with a b.p. below 100° and a sp. gr. of 1.9 at 0°.	$GeCl_4$ a liquid with a b.p. of 86°, and a sp. gr. at 18° of 1.887.
EsF_4 not gaseous.	$GeF_4.3\,H_2O$ a white solid.
Es forms a compound $Es(C_2H_5)_4$ boiling at 160°, and with a sp. gr. 0.96.	Ge forms a compound $Ge(C_2H_5)_4$ boiling at 160° and with a sp. gr. slightly less than water.

4. *Correction of Atomic Weights.* When an element falls in a position in the periodic table where it clearly does not belong, suspicion as to the correctness of its atomic weight is immediately aroused. Frequently a redetermination of the atomic weight has revealed an error which, when corrected, has resulted in assigning the element to a place among its analogues. Formerly the accepted atomic weights of osmium, iridium, platinum and gold were in the order

$$\mathrm{Os} > \mathrm{Ir} > \mathrm{Pt} > \mathrm{Au}.$$

But from analogies existing between osmium, ruthenium and iron and the disposition of the preceding members of Group VIII, Mendeléeff predicted that the atomic weights were in error and that the order of the elements should be

$$\mathrm{Os} < \mathrm{Ir} < \mathrm{Pt} < \mathrm{Au}.$$

Subsequent atomic weight determinations by Seubert substantiated Mendeléeff's prediction.

Defects in the Periodic Law. While the arrangement of the elements in the periodic table is on the whole very satisfactory, there are several serious defects in the system which should be pointed out. At the very outset there is difficulty in finding a place for hydrogen in the system. The element is univalent and falls either in Group I, with the alkali metals, or in Group VII with the halogens. While the element is electro-positive it cannot be considered to possess metallic properties. It forms hydrides with some of the metallic elements and can be displaced by the halogens from organic compounds. These facts make it extremely difficult to decide whether hydrogen should be placed in Group I or Group VII. The idea has been advanced that hydrogen is the only known member of the first series of the periodic table.

These hypothetical elements have been styled *proto-elements*, the successive members of the series being, proto-glucinum, proto-boron and so on to the last element in the series, proto-fluorine. To find a suitable location for the rare-earth elements in the periodic system is another difficulty which has not been satisfactorily met. Brauner considers that these elements should all be grouped together with cerium (at. wt. = 140.25), but owing to our limited knowledge of the properties of these elements it seems better to defer attempting to place them for the present. In the group of non-valent elements the atomic weight of argon is distinctly higher than that of potassium in the next group. There can be little doubt that the values of the atomic weights are correct and it is evidently impossible to interchange the positions of these two elements in the periodic table, since argon is as much the analogue of the rare gases as potassium is of the alkali metals. A similar discrepancy occurs with the elements, tellurium and iodine. The atomic weight of the former element is appreciably higher than that of the latter and, notwithstanding the attempts of numerous investigators to prove tellurium to be a complex of two or more elements, nothing but failure has attended their efforts. Still another anomaly is encountered in Group VII, where manganese is classed with the halogen family, to which it bears much less resemblance than it does to chromium and iron, its two immediate neighbors.

As has already been mentioned, Group VIII is made up of nonconformable elements. If the properties of the elements are dependent upon their atomic weights, it should be impossible for several elements having almost identical atomic weights and different properties to exist, and yet such is the case with the elements of Group VIII. The elements copper, silver and gold, while not closely resembling the other members of Group VIII, are much more closely allied to them than to the alkali metals with which they are also classed. Notwithstanding its imperfections, the periodic law must be regarded as a truly wonderful generalization which future investigations will undoubtedly show to be but a fragment of a more comprehensive law.

Brink

CHAPTER III.

THE ELECTRON THEORY.

Conduction of Electricity through Gases. Within recent years the discovery of new facts relative to the conduction of electricity through gases has led to the development of the so-called *electron* or *corpuscular theory of matter*. Under ordinary conditions gases are practically non-conductors of electricity, but when a sufficiently great difference of potential is established between two points within a gas it is no longer able to withstand the stress, and an electric discharge takes place between the points. The potential necessary to produce such a discharge is quite high, several thousand volts being required to produce a spark of one centimeter length in air at ordinary pressures. The pressure of the gas has a marked effect upon the character of the discharge and the potential required to produce it. If we make use of a glass vessel similar to that shown in Fig. 3, the effect of pressure on the nature of the discharge may be studied.

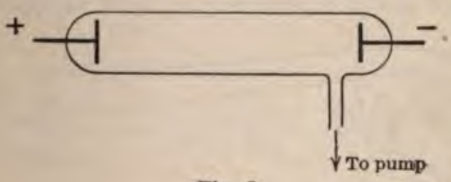


Fig. 3.

This apparatus consists of a straight glass tube about 4 cm. in diameter and 40 cm. long, into the ends of which platinum electrodes are sealed. To the side of the vessel a small tube is sealed so that connection may be established with an air-pump and manometer. If the electrodes are connected with the terminals of an induction coil and the pressure within the tube be gradually diminished, the following changes in the character of the discharge will be observed. At first the spark becomes more uniform and then broadens out, assuming a bluish color. When a pressure of about 0.5 mm. is reached, the negative electrode or *cathode* will appear to be surrounded by a thin luminous layer; next to this will be a dark region, known as the *Crookes' dark space;* adjoining this will be a luminous portion, called the *negative glow,* and beyond this will be seen another dark region which is frequently referred to as the *Faraday dark space.* Between the Faraday dark space and the positive electrode or *anode* is a luminous portion, called the *positive column.* By a slight variation of the current and pressure the positive column can be caused to break up into alternate light and dark spaces or *striæ,* the appearance of which is dependent upon various factors such as the nature of the gas and the size of the tube. If we use a modification of this tube, such as is shown in Fig. 4, and diminish the pressure to about 0.01 mm., a new phenomenon will be observed. The positive column will vanish and the walls of the tube opposite the cathode will become faintly phosphorescent. The color of the phosphorescence will depend upon the nature of the glass: if the tube is made of soda glass, the glow will be greenish yellow, while with lead glass the phosphorescence will be bluish. The phosphorescence is due to the bombardment of the walls of the

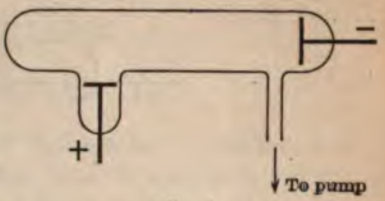


Fig. 4.

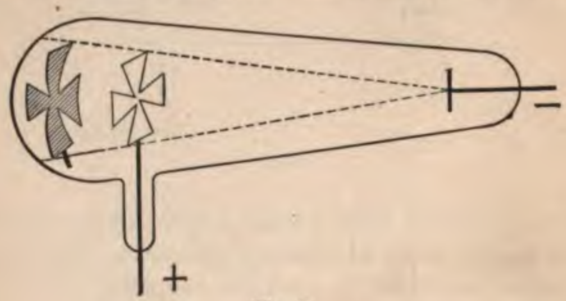


Fig. 5.

tube by very minute particles projected normally from the cathode. These streams of particles are called the *cathode rays*.

Some Properties of Cathode Rays. The following are among the most important properties of the cathode rays: —

1. *The cathode rays travel in straight lines normal to the cathode: and they cast shadows of opaque objects placed in their path.* This property may be demonstrated by means of the apparatus shown in Fig. 5, where a small metallic Maltese cross is interposed in the path of the rays, a distinct shadow being cast on the opposite wall of the tube. The cross may be hinged at the bottom so that it can be dropped out of the path of the rays, when the usual phosphorescence will be obtained.

2. *The cathode rays can produce mechanical motion.* By means of the apparatus due to Sir William Crookes, Fig. 6, this property of the cathode rays may be demonstrated. Within the vacuum tube is placed a small paddle wheel which rolls horizontally on a pair of glass rails. When the current is applied to the tube, the wheel will revolve, moving away from the cathode. By reversing the current, the wheel will stop and then rotate in the opposite direction owing to the reversal of the direction of the cathode stream.

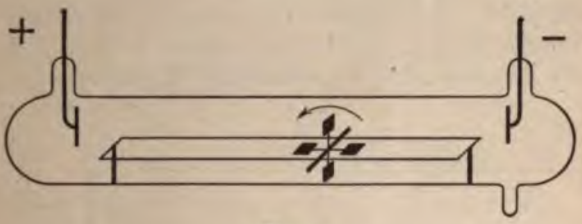


Fig. 6.

3. *The cathode rays cause a rise of temperature in objects upon which they fall.* In the tube shown in Fig. 7, the anode consists of a small piece of platinum: this is placed at the center of curvature of the spherical cathode. After pumping down to the proper pressure, if a strong discharge be sent through the tube,

the anode will begin to glow, and if the action of the current be continued long enough, the platinum plate may be rendered incandescent, thus showing the marked heating effect of the cathode rays.

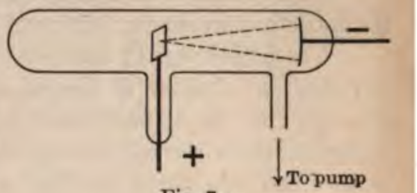


Fig. 7.

4. *Many substances become phosphorescent on exposure to the cathode rays.* If the cathode rays be directed upon different substances, such as calc-spar, barium platino-cyanide, willemite, scheelite and various kinds of glass, beautiful phosphorescent effects may be observed. This phosphorescent property is useful in observing and experimenting with the cathode rays.

5. *The cathode rays can be deflected from their rectilinear path by a magnetic field.* In studying the magnetic deviation of the cathode rays a tube similar to that shown in Fig. 8 has been found very satisfactory. An aluminium diaphragm, *A*, pierced with a 1 mm. hole, is placed in front of the cathode while at the opposite end of tube is placed a phosphorescent screen, *D*. When the discharge takes place a circular phosphorescent spot will appear on *D*. If the tube be placed between the poles of an electromagnet, the phosphorescent spot will move at right angles to the direction of the magnetic field. On reversing the polarity of the magnet the spot will move in the opposite direction. Furthermore the direction of the deflection will be found to be

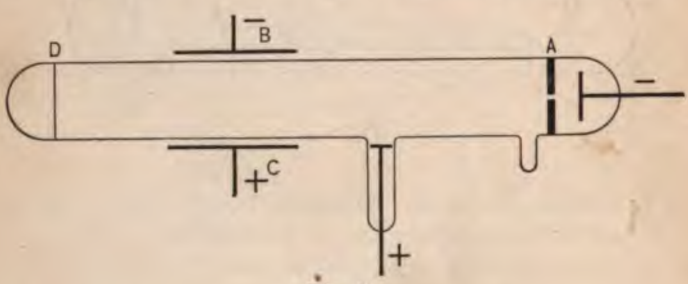


Fig. 8.

similar to that produced by a negative charge of electricity moving in the same direction as the cathode ray.

6. *The cathode rays can be deflected from their rectilinear path by an electrostatic field.* The same tube which was used in observing the magnetic deflection may be employed in studying the effect of an electrostatic field. Two insulated metal plates, *B* and *C*, are placed on opposite sides of the tube and parallel to each other. When the tube is in action, if a difference of potential of several hundred volts be applied to the plates, the phosphorescent spot on *D* will be found to move, the direction of the motion being the same as that of a negatively charged body under the influence of an electrostatic field. Reversal of the field causes the phosphorescent spot to move to the opposite side of the screen.

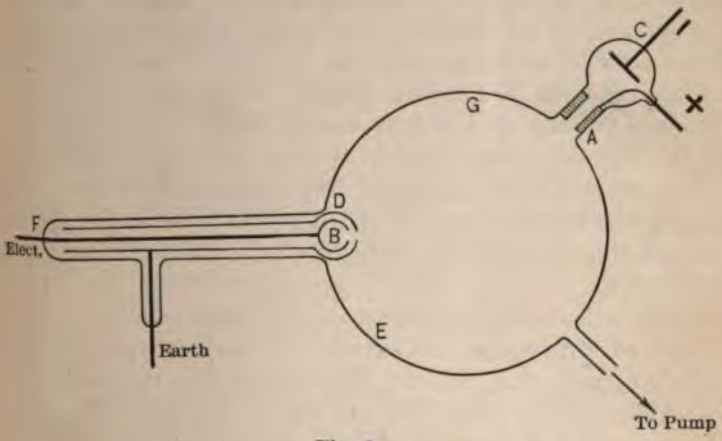


Fig. 9.

7. *The cathode rays carry a negative charge.* Probably the most important characteristic of the cathode rays is their ability to carry a negative charge. While the magnetic and electrostatic deviation of the rays made this fact more than probable, it remained for Perrin to demonstrate that a negative electrification accompanies the cathode stream. A modification of Perrin's apparatus due to J. J. Thomson is shown in Fig. 9. It con-

sists of a spherical bulb to which is sealed a smaller bulb and a long side tube. The small bulb contains the cathode *C* and the anode *A*. The anode consists of a tight-fitting brass plug pierced by a central hole of small diameter. The side tube, which is out of the direct range of the cathode rays, contains two coaxial metallic cylinders insulated from each other, each being perforated with a narrow transverse slit: *D* is earth-connected and *B* is connected with an electrometer by means of the rod *F*. When the tube has been pumped down to the proper pressure for the production of cathode rays, a phosphorescent spot will appear at *E* directly opposite the cathode *C*. Upon testing *B* for possible electrification by means of the electrometer, it will be found to be uncharged. If the cathode stream be deflected by means of a magnet so that the rays fall upon *B*, a sudden charging of the electrometer will be observed, proving that *B* is becoming electrified. Upon deflecting the rays still further so that they are no longer incident upon *B*, the accumulation of charge will immediately cease. If the electrometer be tested for polarity, it will be found to be negatively charged, thus proving the charge carried by the cathode rays to be negative.

8. *The cathode rays can penetrate thin sheets of metal.* In 1894 Lenard constructed a vacuum tube fitted with an aluminium window opposite the cathode. He showed that the cathode rays passed through the aluminium and are absorbed by different substances outside of the tube, the absorption varying directly with the density of the substance.

9. *The cathode rays when directed into moist air cause the formation of fog.* This phenomenon has been shown by C. T. R. Wilson to be due to the minute particles in the cathode stream acting as nuclei upon which the water vapor can condense.

Velocity of the Cathode Particle. Since the cathode rays consist of minute, negatively-charged particles which can be deflected by a magnetic and an electrostatic field, it is possible to measure their speed and to compute the ratio of the mass of a particle to its charge. The special form of tube shown in Fig. 10 was devised for the purpose by J. J. Thomson. It consists of a glass tube about 60 cm. in length, furnished with a flat circular cathode, *C*, and an anode, *A*, in the form of a cylindrical brass plug about 2.5 cm. in length, pierced by a central hole 1 mm. in diameter. Another brass plug, *B*, is placed about 5 cm. away from *A*, the two holes being in exactly the same straight line, so that a very narrow bundle of rays may pass along the axis of the tube and fall upon the phosphorescent screen at the opposite end of the tube. Upon this screen is a millimeter scale, *SS′*. Two parallel plates, *D* and *E*, are sealed into the tube for the purpose of establishing an electrostatic field. When the tube is connected with an induction coil or other source of high-potential, a phosphorescent spot will appear at *F*. If a strong magnetic field be applied, the lines of force being at right angles to the plane of the diagram, the rays will be deflected vertically and the spot on the screen will move from *F* to *G*.

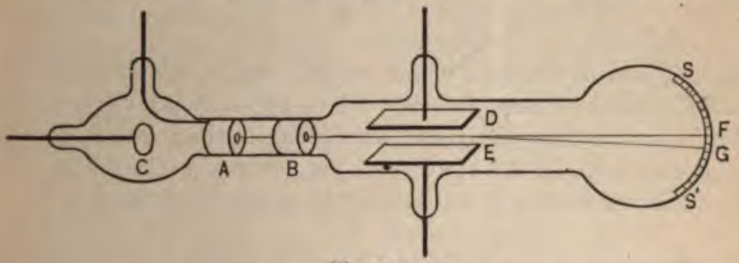


Fig. 10.

Let *H* denote the strength of the magnetic field and let *m*, *e* and *v* represent respectively the mass, charge and velocity of a cathode particle. A magnetic field, *H*, acting at right angles to the line of flight of the cathode particle will exert a force, *Hev*, which will tend to deflect the particle from a rectilinear path. This force must be equal to the centrifugal force of the moving particle acting outwards along its radius of curvature. Therefore

$$Hev = \frac{mv^2}{r},$$

or

$$Hr = \frac{mv}{e}. \tag{1}$$

Since H and r can both be measured, the ratio, $\frac{mv}{e}$, can be determined. Now if a difference of potential be established between D and E, and the lines of force in the electrostatic field have the proper direction, it will be possible to alter the strength of the field so as to just counterbalance the effect of the magnetic field, and bring the phosphorescent spot back to F again. Under these conditions, if X denotes the strength of the electrostatic field, we have

$$Xe = Hev,$$

or

$$v = \frac{X}{H}. \tag{2}$$

Since X and H can both be measured, v can be calculated, and by introducing the value so obtained into equation (1), the ratio e/m can be evaluated. By this method the average value of v has been found to be 2.8×10^9 cm. per second, while 1.7×10^7 is the mean value of a large number of determinations of the ratio e/m.

Comparison of the Ratio of Charge to Mass for the Cathode Particle with that for the Ion in Electrolysis. The ratio of the charge carried by an ion in electrolysis to its mass can be easily computed. Thus it may be shown that the ratio of the charge E, of the hydrogen ion to its mass, M, in electrolysis is about 1×10^4 C.G.S. units or

$$\frac{E}{M} = 1 \times 10^4 \text{ approximately.}$$

The mass of the hydrogen ion may be considered to be identical with that of the hydrogen atom, the lightest atom known. Comparing the value of e/m for the cathode particle with the value of E/M for the hydrogen ion in electrolysis, it is evident that the former is about 1700 times greater than the latter.

Charge Carried by the Cathode Particle. Until the value of the charge carried by the cathode particle has been determined, it is clearly impossible to compute its mass. Thus, if we consider the last statement of the preceding paragraph, which may be formulated as follows: —

$$e/m : E/M :: 1700 : 1,$$

the proportion will remain unaltered whether $m = M/1700$ and $e = E$, or $e = 1700$ and $m = M$. The method employed to determine the charge carried by a cathode particle is too complicated for a detailed description in this place; merely the general outline will be given. Upon suddenly expanding a volume of saturated water vapor, its temperature is lowered, and a cloud forms, each particle of dust present serving as a nucleus for a fog particle. If sufficient time be allowed for the mist to settle and the vapor to become saturated again, a repetition of the preceding process will result in the formation of less mist, owing to the presence of fewer dust particles. By repeating the operation enough times the space may be rendered dust free. As has already been pointed out, cathode particles serve as nuclei for the condensation of water vapor, their function being similar to that of dust particles. It has been shown by Sir George G. Stokes that if a drop of water of radius r, be allowed to fall through a gas of viscosity η, then the velocity with which the drop falls is given by the equation

$$v = \frac{2}{9} \cdot \frac{gr^2}{\eta}, \tag{3}$$

where g is the acceleration due to gravity. The viscosity of air at any temperature being known, a cloud can be produced in an appropriate chamber by expansion of water vapor in the presence of cathode particles and the speed, v, with which the cloud falls can be measured, and hence r can be calculated by means of equation (3). If m is the total mass of the cloud and n is the number of drops per cubic centimeter, then

$$m = 4/3\, n\pi r^3 \text{ (density of water = 1).}$$

From a simple application of thermodynamics m may be determined. Knowing the values of m and r, the number of drops in the cloud, n, which is the same as the number of cathode particles, can be calculated. It is a simple matter to measure the total charge in the expansion chamber, and dividing this by the total number of charged particles, gives the charge carried by a single particle. The latest determinations of J. J. Thomson show this to be $3.4 \times {}^{-10}$ electrostatic unit. This is practically identical with the calculated value of the charge on the hydrogen ion in electrolysis, or $e = E$ and therefore $m = M/1700$; the mass of the cathode particle is 1/1700 of the mass of the atom of hydrogen. The cathode particle has the smallest mass yet known and has been called the *corpuscle* or *electron*.

An ingenious modification of the foregoing method devised by Millikan,* has made it possible to determine e with extreme accuracy. Millikan gives as the mean of a large number of determinations of e, the following value which he states is in error by less than 0.1 per cent:

$$e = 4.4775 \times 10^{-10} \text{ electrostatic units.}$$

For purposes of comparison, the following values of e obtained by other investigators using different experimental methods are here given: —

(*a*) Making use of available data on radiant energy, Planck calculated $e = 4.69 \times 10^{-10}$.

(*b*) By counting the number of scintillations produced by a known weight of polonium and measuring the total charge, Regener found $e = 4.79 \times 10^{-10}$.

(*c*) By counting the number of α-particles escaping from a given amount of radium bromide and measuring the total charge, Rutherford and Geiger calculated $e = 4.65 \times 10^{-10}$.

The Avogadro Constant. The actual number of molecules in one gram-molecule or the actual number of atoms in one gram-atom of a gas is called the *Avogadro Constant*. The most accurate method for the calculation of this constant involves the elementary charge of electricity, e.

The quantity of electricity carried by one gram equivalent in electrolysis has been found to be 96,500 coulombs (see p. 390). This quantity, known as the faraday, and commonly designated by F, bears the same relation to e that the actual weight of an atom bears to the number expressing its atomic weight. The relation between the Avogadro constant N and the ionic and electronic charges F and e, is given by the equation

---

* Phil. Mag., 6, **19**, 209 (1910); Phys. Rev., **39**, 349 (1911); Trans. Am. Electrochem. Soc., **21**, 185 (1912).

$$N = \frac{F}{e}.$$

Substituting the above values in this equation and converting coulombs into electrostatic units, we have

$$N = \frac{96500 \times 3 \times 10^{9}}{4.4775 \times 10^{-10}} = 64.6 \times 10^{22}.$$

Other Sources of Electrons. Electrons may be produced by other agents than cathode rays. Thus, electrons are emitted by radium and other radioactive substances, by metals and amalgams under the influence of ultra-violet light, and also by gas flames charged with the vapors of salts. It has been shown that from whatever source an electron is derived, the value of the ratio e/m remains constant. This interesting fact has led Thomson to suggest that the electron may be regarded as "one of the bricks of which the atom is built up."

Before entering upon a discussion of modern views of atomic structure, however, it will be necessary to summarize very briefly some of the salient facts of radiochemistry.

CHAPTER IV.

RADIOACTIVITY.

Discovery of Radioactivity. The first radioactive substance was discovered by Henri Becquerel * in 1896. It had been shown by Roentgen in the previous year that the bombardment of the walls of a vacuum tube by the cathode stream, gives rise to a new type of rays, which, because of their puzzling characteristics, he called X-rays. The portion of the tube where these rays originate was observed to fluoresce brilliantly, and it was at once assumed that this fluorescence might be the cause of the new type of radiation.

Many substances were known to fluoresce under the stimulus of the sun's rays, and it was natural, in the light of Roentgen's discovery, that all substances which exhibit fluorescence should be subjected to careful examination. Among those who became interested in these phenomena was Becquerel. He studied the action of a number of fluorescent substances, among which was the double sulphate of potassium and uranium. This salt, after exposure to sunlight, was found to emit a radiation capable of affecting a carefully protected photographic plate. Further investigation proved that the fluorescence had nothing to do with the photographic action, since both uranous and uranic salts were found to exert similar photographic action, notwithstanding the fact that uranous salts are not fluorescent. The photographic activity of both uranous and uranic salts was found to be proportional to their content of uranium. Becquerel also showed that preliminary stimulation by sunlight was wholly unnecessary. Uranium salts which had been kept in the dark for years were found to be just as active as those which had been recently exposed to brilliant sunlight. The properties of the rays emitted by uranium salts differ in many respects from those of the X-rays. The rate of emission of the uranium rays remains unaltered at the highest or the lowest obtainable temperatures. The entire behavior of these salts justifies the conclusion that the continuous emission of penetrating rays is a specific property of the element uranium itself. This property of spontaneously emitting radiations capable of penetrating substances opaque to ordinary light is called *radioactivity.*

---

* Compt. rendus, **122**, 420 (1896).

Discovery of Radium. Shortly after the discovery of the radioactivity of uranium, the element thorium and its compounds were also found to be radioactive. As a result of a systematic examination by Mme. Curie * of minerals known to contain uranium or thorium, it was learned that many of these were much more radioactive than either uranium or thorium alone. Thus, pitchblende, one of the principal ores of uranium, was found to be four times more active than uranium alone, and chalcolite, a phosphate of copper and uranium, was found to be at least twice as active as uranium. On the other hand, when a specimen of artificial chalcolite, prepared in the laboratory from pure materials, was examined, its activity was found to be proportional to the content of uranium. Mme. Curie concluded from this result that natural chalcolite and pitchblende must contain a minute amount of some substance much more active than uranium.

With the assistance of her husband, Mme. Curie undertook the task of separating this unknown substance from pitchblende. Pitchblende is an extremely complex mineral and its systematic chemical analysis calls for skill and patience of a high order. Without entering into details as to the analytical procedure, it must suffice here to state the results obtained. Associated with bismuth, a very active substance was discovered, to which Mme. Curie gave the name polonium in honor of her native land, Poland. In like manner, an extremely active substance was found associated with barium in the alkaline earth group. The substance was called radium because of its great radioactivity.

While the isolation of pure polonium is extremely difficult and, while sufficient quantities have not been obtained to permit determinations of its physical properties, the isolation of radium in relatively large amounts is readily accomplished. The pure bromides of radium and barium are prepared together and the two salts are then separated by a series of fractional crystallizations. That the salts of barium and radium are very similar in chemical properties is shown by the fact that they separate together from the same solution. The atomic weight of radium has been determined by several investigators, the accepted value being 226. It is thus, with the exception of uranium, the heaviest known element.

---

* Compt. rendus, 126, 1101 (1898).

In 1910, Mme. Curie * succeeded in obtaining metallic radium. It is a metal possessing a silvery luster, dissolving in water with energetic evolution of hydrogen and tarnishing rapidly in air with the formation of the nitride.

It is estimated that one ton of pitchblende contains approximately 0.2 gram of radium.

Other Radioactive Substances. Shortly after the discovery of radium and polonium by the Curies, Debierne † discovered another radioactive element in pitchblende. This element, which he named actinium, was found associated with the iron group in the course of the analysis of the mineral.

In 1906, Boltwood ‡ discovered in pitchblende, and in several other uranium minerals, the presence of still another radioelement which he named ionium. Ionium is much more active than thorium to which it bears such a close resemblance that the two elements cannot be separated from each other.

The lead which is obtained from uranium and thorium minerals is found to be slightly radioactive, the activity being attributed to the presence of a small proportion of a constituent called radiolead, the chemical properties of which resemble those of ordinary lead. It is interesting to note that recent determinations by Richards § of the atomic weight of lead obtained from different sources, reveal differences greater than the possible experimental errors of the determinations. Thus, the values of the atomic weight of lead from pitchblende and from thorite were found to be 206.40 and 208.4 respectively, while the value of the atomic weight of ordinary lead is 207.15.

---

* Compt. rendus, **151**, 523 (1910).

† Compt. rendus, **129**, 593 (1899).

‡ Am. Jour. Sci., **22**, 537 (1906).

§ Jour. Am. Chem. Soc., **36**, 1329 (1914).

About thirty other radioactive substances have been separated and many of their properties have been determined. All of these radio-elements have been shown to be the lineal descendants of one or the other of the two parent elements, uranium or thorium.

Ionization of Gases. The radiations emitted by radioactive substances have the power of rendering the air through which they pass conductors of electricity. To account for this action, Thomson and Rutherford formulated the theory of gaseous ionization. According to this theory, which has since been experimentally confirmed, the radiations break up the components of the gas into positive and negative carriers of electricity called *ions*. If two parallel metal plates are connected to the terminals of a battery and a radioactive substance is placed between them, the air will be ionized and, owing to the movement of the positive and negative ions toward the plates of opposite sign, an electric current will pass between the plates. If the electric field is weak, the mutual attraction between the positive and negative ions will cause many of them to recombine before reaching the plates and the resulting current will be small. As the strength of the field is increased, the greater will be the speed of the ions toward the plates and the smaller will become the tendency to recombination. Ultimately, with increasing strength of field all of the ions will be swept to the plates as fast as they are formed and the ionization current will attain a maximum value. This limiting or *saturation current* affords the most accurate method for the measurement of radioactivity.

The method is so sensitive that, by means of it alone, it is possible to detect amounts of radioactive products far beyond the reach of the balance or the spectroscope. The theory of gaseous ionization has been confirmed in several different ways, but one of the most striking verifications of the theory is that due to C. T. R. Wilson. Making use of the fact that the ions tend to condense water vapor around themselves as nuclei, Wilson succeeded in actually photographing the path of an ionizing ray in air.

Photographic Action of Radiations. It has already been pointed out that the radiations from radioactive substances are capable of affecting a photographic plate. The photographic action of the radiations has been employed quite extensively in studying radioactive phenomena from a purely qualitative standpoint. The method employed, consists in exposing the photographic plate, which has been previously wrapped in opaque black paper, to the action of the radiations. The time of exposure varies with the nature of the substance under examination, a few minutes being required for highly active preparations while several days or even weeks may be needed for preparations of low activity.

Phosphorescence Induced by Radiations. A screen covered with crystals of phosphorescent zinc sulphide is rendered luminous when exposed to fairly intense radiation from a radioactive substance. This phenomenon has been shown to be due to the bombardment of the crystals of zinc sulphide by the so-called α-rays (see below). When the screen is examined with a lens the phosphorescence is seen to consist of a series of scintillations of very short duration.

Nature of the Radiations. The ionizing, photographic, and luminescent properties of the radiations from radioactive substances are not sufficient to differentiate them from cathode rays or X-rays, although each of these properties may be employed in determining their intensity.

Evidence of the composite character of the radiations was furnished by a study of their penetrating power as well as by investigations of the behavior of the rays when subjected to the action of magnetic and electric fields.

A thin sheet of aluminum or a few centimeters of air was found sufficient to cut off a large percentage of the rays.

The unabsorbed portion of the radiation was found to consist of two distinct types, one of which was cut off by five or six millimeters of lead while the other possessed such great penetrating power that its presence could be readily detected after passing through a layer of lead fifteen centimeters thick.

Rutherford named these three distinct types of radiation, the α-, β-, and γ-rays, respectively. The penetrating powers of the α-, β-, and γ-rays may be approximately expressed by the proportion 1 to 100 to 10,000; *i.e.*, the β-rays are 100 times more penetrating than the α-rays, while the γ-rays are 100 times more penetrating than the β-rays.

The general characteristics of the three kinds of rays may be briefly summarized as follows: —

(1) *α-Rays.* The α-rays consist of positively charged particles moving with speeds approximately one-tenth as great as that of light. These particles have been shown to be identical with helium atoms carrying two positive charges of electricity. They are appreciably deflected from a rectilinear path by magnetic and electric fields. They possess great ionizing power but relatively little penetrating power or photographic action. The depth to which an α-particle penetrates a homogeneous absorbing medium before losing its ionizing power, is known as its "range." The range is proportional to the cube of the initial speed of the α-particle and is one of the characteristic properties of the radio-elements emitting α-rays.

(2) *β-Rays.* The β-rays consist of negatively charged particles moving with speeds varying from two-fifths to nine-tenths of the speed of light. They are, in fact, electrons moving with much greater speeds than those shot out from the cathode in a vacuum tube. While the α-particles emitted by a particular radio-element have a definite velocity, the corresponding β-ray emission consists of a flight of particles having widely different speeds. The penetrating power of the β-rays is conditioned by the speed of the particles, those which move most rapidly possessing the greatest penetrating power.

The ionizing action of the β-rays is much weaker than that of the α-rays, while exactly the reverse is true of the photographic action.

(3) *γ-Rays.* The γ-rays are identical with X-rays. They consist of extremely short waves of light, the wave-length varying from about 1×10^{-8} cm. for the rays of low penetrating power to about 1×10^{-9} cm. for the most penetrating rays. Obviously the γ-rays cannot be deflected from a rectilinear path by either electric or magnetic fields.

Uranium-X and Thorium-X. In 1900, Crookes [*] precipitated a solution of a uranium salt with ammonium carbonate; when an excess of the reagent had been added, all but a minute portion of the precipitate was found to have dissolved. This small insoluble residue, though chemically free from uranium, was found, when tested photographically, to be several hundred times more active, weight for weight, than the original salt. The solution, on the other hand, was found to have lost nearly all of its activity. At the end of a year, however, the solution had entirely regained its original activity, while the insoluble residue had become inactive. The active substance thus separated was called, on account of its unknown nature, uranium-X.

---

[*] Proc. Roy. Soc., **64,** 409 (1900).

Similarly, Rutherford and Soddy,* by precipitating a solution of a thorium salt with ammonium hydroxide, found that a large proportion of the activity remained behind in the thorium-free filtrate. On evaporating the filtrate to dryness and driving off the ammonium salts, a residue was obtained which was, weight for weight, several thousand times more active than the original solution. After standing for a month, this residue was found to have lost its activity, while the precipitate had regained the activity of the original thorium compound. This active residue was called thorium-X from analogy to Crookes' uranium-X.

The fact that uranium-X and thorium-X had each been obtained as the result of specific chemical processes, seemed to warrant the conclusion that they are new substances possessing well-defined properties. The manner in which these substances were obtained led to a variety of speculations as to the mechanism of the process involved in their production. In a subsequent paragraph it will be shown that the so-called disintegration theory offers a most satisfactory explanation of the foregoing experimental results.

The Emanations. The element thorium was found by Rutherford to give off a radioactive gas or emanation which, when left to itself, rapidly loses its activity in a similar manner to uranium-X and thorium-X. The thorium emanation was found to resemble the inactive gases in its chemical behavior. Thus, it can be subjected to the action of lead chromate, metallic magnesium and zinc dust at extremely high temperatures without undergoing change. The only other substances which, at the time of the discovery of the emanation, were known to resist the action of these reagents under the same conditions were the gaseous elements helium, neon, argon, krypton, and xenon. The most conclusive evidence of the gaseous character of the thorium emanation is the fact that it condenses to a liquid at very low temperatures.

---

* Phil. Mag., VI, 4, 370 (1902).

Rutherford and Soddy showed that the origin of the thorium emanation is thorium-X and not the element thorium itself. Freshly precipitated thorium hydroxide shows only a trace of emanating power, whereas the thorium-X separated from the filtrate possesses this power to a marked degree. As the thorium-X gradually loses its emanating power, the hydroxide shows a corresponding recovery.

Radium was found to give off an emanation which behaves similarly to the thorium emanation except that it parts with its activity at a slower rate. The rate at which the radium emanation is produced, together with its longer life, enabled Ramsay and Soddy * not only to measure the volume of the emanation obtained from 60 mg. of radium bromide but also to establish the fact that it obeys Boyle's law.

The Active Deposits. It was discovered by Rutherford † for thorium, and by M. and Mme. Curie ‡ for radium, that the emanations from these elements are capable of imparting radioactivity to surrounding objects. On the other hand, uranium and polonium, which evolve no emanations, have no such influence on their environment. This fact is taken as a proof that induced radioactivity is due to actual contact with the emanations. If a negatively charged platinum wire be exposed to the thorium or radium emanation, the whole of its activity will be concentrated on the wire. This so-called *active deposit* may be transferred from the wire to a piece of sandpaper by rubbing. It may be sublimed from the wire to the walls of the tube in which it is heated, or it may be dissolved from the wire by means of hydrochloric or sulphuric acid. On evaporating the solution, the activity will be found to reside on the evaporating dish. Microscopic examination of the wire fails to reveal any deposit, and the most sensitive balance is incapable of detecting any gain in weight after exposing the wire to the emanation. These experiments leave no room for doubt that the active deposits consist of infinitesimal amounts of solid substances possessing definite chemical properties. The active deposits undergo a gradual loss of activity similar to that observed with the emanations and with uranium-X and thorium-X.

---

* Proc. Roy. Soc., **73**, 346 (1904).

† Phil. Mag., VI, **22**, 621 (1911).

‡ Compt. rendus, **129**, 714 (1899).

The Disintegration Hypothesis. It was soon discovered that the active deposits undergo a series of additional radioactive changes. These subsequent transformations were found to be much more obscure and difficult to follow. In fact, it is only because of the ingenuity and mathematical acumen of those who undertook this difficult research that we are today in possession of such complete knowledge of the succeeding members of the radioactive series of elements.

In 1903, Rutherford and Soddy * brought forward their theory of atomic disintegration which affords a perfectly satisfactory interpretation of the complicated results already detailed, as well as of the subsequent changes in the active deposits to which reference has just been made. According to this theory, radioactive change is assumed to be due to the spontaneous disintegration of the radio-elements with concomitant formation of new elements. These new elements, which are often less stable than the parent element, are assumed to undergo further disintegration with the production of still other elements, the end of the process ultimately being reached when a stable element is formed.

The Radioactive Constant. The activity of a radio-element decays exponentially with time according to the equation —

$$I_t = I_0 e^{-\lambda t}, \qquad (1)$$

where I_0 is the initial activity, I_t the activity at the end of an interval of time t, λ a constant, and e is the base of the natural system of logarithms. The constant λ, known as the *radioactive constant*, represents the fraction of the total amount of radioactive substance undergoing disintegration in unit of time, provided the latter is so small that the quantity at the end of the time unit is only slightly different from the initial quantity. The reciprocal of the radioactive constant is called the *average life* of the element. Soddy defines the average life of a radio-element as "the sum of the separate periods of future existence of all the individual atoms divided by the number in existence at the starting point."

---

* Phil. Mag., VI, 5, 576 (1903).

If n_t represents the number of atoms of a radio-element changing in unit time at the end of a time t, and n_0 the corresponding value when $t = 0$, equation (1) may be written

$$n_t = n_0 e^{-\lambda t}.$$

In order to determine the initial rate of change, let N_0 denote the total number of atoms originally present, and N_t the number remaining unchanged at time t; we then have

$$N_t = \int_t^\infty n_t dt = \frac{n_0}{\lambda} e^{-\lambda t}.$$

But when $t = 0$, $N_0 = N_t$

and $$N_0 = \frac{n_0}{\lambda}.$$

Hence $$N_t = N_0 e^{-\lambda t}.$$

On differentiating, we have

$$\frac{dN}{dt} = -\lambda N. \tag{2}$$

Or, stated in words, the rate at which the atoms of a radio-element undergo disintegration at any given time is found to be proportional to the total number in existence at that time.

This law of radioactive change is also peculiar to unimolecular chemical reactions (see p. 361). The velocity of a unimolecular reaction, however, is conditioned by the temperature, whereas the velocity of a radioactive change remains unaltered at the highest and the lowest attainable temperatures.

The time required for one-half of a radio-element to undergo transformation is known as the *period of half change* T, and may be readily calculated from λ as follows: —

$$\log 0.5 = 0.4343\,\lambda T$$

or $$T = \frac{0.6932}{\lambda}.$$

It has been shown by Geiger and Nuttall * that the radioacti constant λ and the range R of the α-particles shot out from a d integrating atom bear the following empirical relation to ea other,

$$\lambda = aR^b,$$

where a and b are constants, the former constant being charact istic of the particular radioactive series to which the element b longs. This formula has been found useful in calculating t values of λ for the longest and shortest lived elements.

Radioactive Equilibrium. It is evident that a state of equ librium must ultimately be attained among the atoms of a radi active substance. When the rate of production of a radio-eleme from its parent element is equal to its rate of disintegration in the next succeeding element of the series, the substance is said be in radioactive equilibrium. The relative amounts of the su cessive members of a series of elements in radioactive equilibriu are inversely proportional to their radioactive constants.

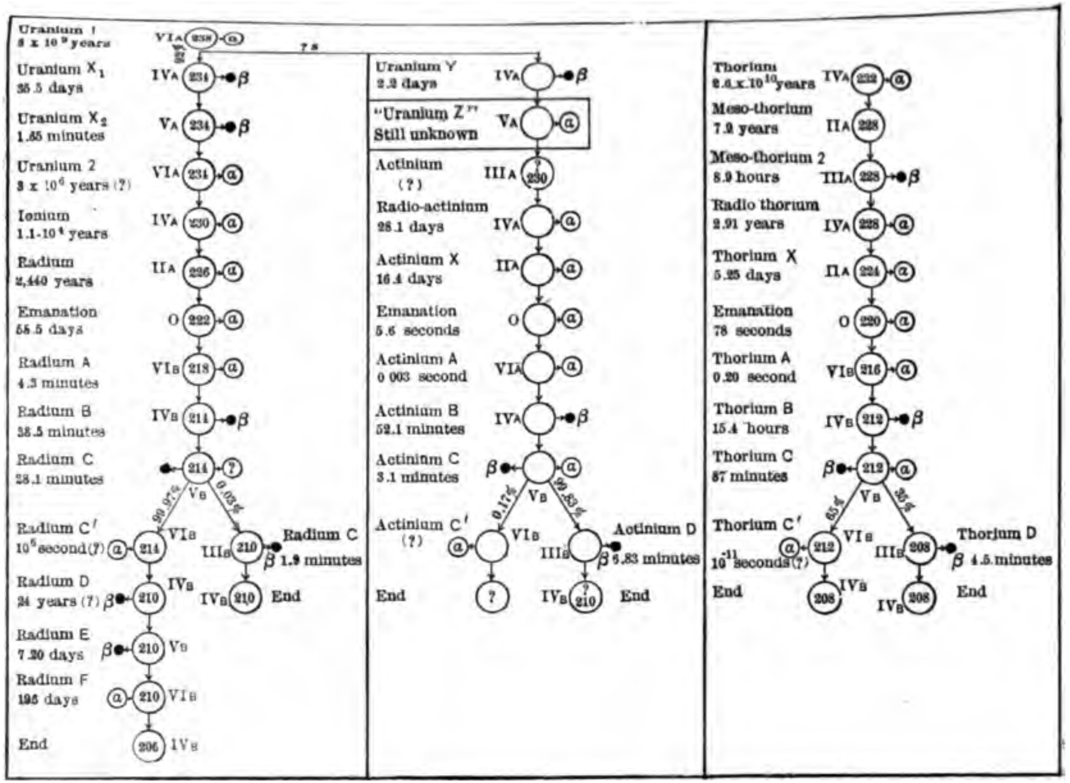
In order that measurements of the rate of radioactive chan may be strictly comparable, it is necessary to make use of t amounts which are in equilibrium with a fixed amount of t parent element. Thus, the unit adopted for the measurement the quantity of the radium emanation is the mass of emanation equilibrium with one gram of radium. This unit is known as t *curie*. Its mass is λ_1/λ_2 gram, where λ_1 and λ_2 are the radioacti constants of radium and its emanation respectively. One cu of radium emanation may be shown to occupy 0.63 cu. mm. und standard conditions of temperature and pressure.

The Disintegration Series. It appears almost certain that t thirty or more radio-elements are disintegration products of one the other of the two parent elements, uranium or thorium. O of the most convenient methods of classification of these elemen is to arrange them in *disintegration series*, starting with the pare element and placing the succeeding elements in the order of th production. The accompanying table shows the three series radio-elements as thus arranged by Soddy. The numbers with the circles are the atomic weights of the elements, while the sm

---

* Phil. Mag., VI, 22, 613 (1911).

TABLE SHOWING DISINTEGRATION SERIES



circles and dots at the right of the larger circles indicate the character of the radiation given out at each stage of the disintegration process. The average life, $1/\lambda$, of each element in the series is given below the name of the element. While a detailed account of the properties of the different radio-elements included in this table cannot be given here, attention should be called to the complex transformations occurring in the active deposit. It is also of interest to observe that the end-products of the three series bear a striking resemblance to the element lead and that their atomic weights are approximately equal and nearly identical with that of ordinary lead.

Counting the α-Particles. It has already been stated that when an α-particle strikes a screen coated with phosphorescent zinc sulphide, a distinct flash of light may be seen when the screen is viewed through a magnifying lens in a dark room. It is obvious that if one could count the number of these scintillations, it would be an easy matter to ascertain the total number of α-particles shot out from a radioactive substance in a given time. By using a phosphorescent screen and a microscope, Regener[*] has determined in this manner the rate of emission of α-particles from polonium. He found from his different experiments an average emission of 3.94×10^5 α-particles per second. The total charge on the α-particles was then measured by collecting them in a suitable measuring vessel. A charge of 37.7×10^{-5} electrostatic units was found to be associated with the total number of α-particles emitted by polonium in one second.

Rutherford and Geiger[†] devised an electrical method for counting the α-particles. In their experiment the source of the α-particles was a small disc which had been exposed to the radium emanation for some hours. This disc was placed in an evacuated tube at a measured distance from a small aperture of known cross-section. The aperture was closed with a thin plate of mica through which the α-particles could pass with ease. After passing through the mica plate, the α-particles entered an ionization chamber filled with air at reduced pressure and fitted with two charged

[*] Sitzunsbericht d. K. preuss. Akad., 38, 948 (1909).

[†] Proc. Roy. Soc. *A*, 81, 141 (1908).

metal plates connected with appropriate apparatus for measuring ionization currents. Whenever an α-particle entered the ionization chamber, a momentary current passed, producing a sudden deflection of the needle of the electrometer. By counting the number of throws of the needle occurring in a definite interval of time, the total number of α-particles passing through the ionization chamber was determined. Knowing the distance of the source of the radiations from the aperture, together with the area of the aperture, the total number of α-particles emitted by the radioactive disc in a given time could be computed. Rutherford and Geiger thus found that one gram of radium emits very nearly 107×10^{16} α-particles per year. Having determined the total number of α-particles emitted, it only remained to measure the total charge, in order to calculate the charge carried by a single α-particle. From a series of very consistent measurements, the charge carried by a single α-particle was found to be 9.3×10^{-10} electrostatic units. Since the fundamental charge e has been shown to be 4.48×10^{-10} electrostatic units, it follows that the α-particle carries two ionic charges of electricity.

Helium Atoms and α-Particles Identical. In 1909, Rutherford and Royds * performed a crucial experiment to determine the nature of the α-particle. A glass bulb was blown with walls thin enough to permit the passage of the α-particles but sufficiently strong to withstand atmospheric pressure. The bulb was filled with radium emanation and then enclosed in an outer glass tube to which a spectrum tube had been sealed. On exhausting the outer tube and examining the spectrum of the residual gas, no evidence of helium was obtained until after an interval of twenty-four hours. After four days the characteristic yellow and green lines were plainly visible and at the end of the sixth day, the complete spectrum of helium was obtained. The unavoidable conclusion from this experiment is, that the presence of helium in the outer tube must have been due to the α-particles which were projected through the thin walls of the inner tube. In another experiment, the inner tube was filled with pure helium under pressure while the exhausted outer tube was examined for helium.

---

* Phil. Mag., VI, 17, 281 (1909).

No trace of helium could be detected spectroscopically even after an interval of several days, thus proving that the helium detected in the first experiment must have resulted from the α-particles which had been shot out from the radium emanation with sufficient energy to penetrate the thin walls of the inner tube. These experiments leave no room for doubt that an α-particle becomes a helium atom when its positive charge is neutralized.

Rate of Production of Helium. The rate of production of helium from the series in equilibrium with one gram of radium has been determined experimentally by Rutherford and Boltwood* to be 156 cu. mm. per year. This result agrees closely with the calculated rate of production, viz., 158 cu. mm. per gram of radium per year.

Energy Evolved by Radium. Curie and Laborde † were the first to call attention to the interesting fact that the temperature of radium compounds was uniformly higher than that of their environment. Careful measurements have shown that one gram of radium evolves heat at the rate of approximately 135 gram-calories per hour. That the greater part of this heat energy is due to the α-particles may be proven by a direct calculation of their mean kinetic energy. The magnitude of the store of energy contained in radium may be realized from the statement, that one gram of radium, before it entirely disappears, evolves an amount of heat energy nearly one million times greater than that evolved in the formation of one gram of water from its elements.

---

* Phil. Mag., VI, **22**, 586 (1911).

† Compt. rendus, **136**, 673 (1904).

CHAPTER V.

ATOMIC STRUCTURE.

The Modern Conception of Atomic Structure. As a result of the investigations of Thomson,* Rutherford,† Nicholson,‡ Bohr,§ and others, a theory of atomic structure has been developed which affords a satisfactory interpretation of many of the important relationships among the chemical elements.

Briefly stated, this theory assumes that the atom consists of a central, positively charged nucleus, surrounded by a miniature solar system of electrons. The investigations of Rutherford and Geiger ‖ show that the character of the deflection of α-particles shot out from radioactive atoms at speeds approximating 20,000 miles per second, and consequently completely penetrating other atoms, is such as to indicate an extremely high concentration of positive electricity on the central nucleus. The central nucleus which is supposed to represent nearly the entire mass of the atom, is thought to be very small in comparison with the size of the atom as a whole. Recent investigations make it appear probable that the maximum diameter of the nucleus of the hydrogen atom is about one one-hundred-thousandth of the diameter commonly attributed to the atom. In commenting on this statement, Harkins says: ¶ — "On this basis the atom would have a volume a million-billion times larger than that of its nucleus, and thus the nucleus of the atom is much smaller in comparison with the size of the atom than is the sun when compared with the dimensions of its planetary system." It is highly probable that the central nucleus is itself made up of a definite number of units of positive electricity together with a small number of attendant electrons.

---

* Phil. Mag., **7**, 237 (1904).

† Popular Science Monthly, **87**, 105 (1915).

‡ Phil. Mag., **22**, 864 (1911).

§ Phil. Mag., **26**, 476, 857 (1913).

‖ Phil. Mag., **21**, 669 (1911).

¶ Science, **66**, 419 (1917).

It is further assumed that the units of positive electricity are hydrogen atoms, each of which has been deprived of one electron. If the mass of an atom is largely due to the presence of hydrogen nuclei, then we should expect Prout's hypothesis to hold and the atomic weights of the elements to be exact multiples of the atomic weight of hydrogen. When we consider, however, that according to electromagnetic theory the total mass of a body composed of positive and negative units is dependent upon the relative positions of these units when packed together, it is evident that the mass of the atom will not necessarily be an exact multiple of the mass of the hydrogen atom.

It has already been pointed out that helium is a product of many radioactive transformations. This fact may be taken as an indication of the extraordinary stability of the helium atom. Because of its stability, the nucleus of this atom has come to be considered as a secondary unit of positive electricity. The nucleus of the helium atom, or the nucleus of an α-particle is assumed to consist of four hydrogen nuclei with two nuclear electrons.

\ **The Atomic Number.** Since the algebraic sum of the positive and negative electrification on an atom must be zero, it follows that the charge resident upon the nucleus must be equal to the number of electrons outside the nucleus. This number, which has come to be recognized as more important and characteristic than the atomic weight, is known as the *atomic number*.

X-Rays and Atomic Structure. The discovery by W. L. Bragg in 1912 that X-rays undergo reflection at crystal surfaces and the subsequent development by Mr. Bragg and his father, W. H. Bragg, of the X-rays pectrometer, has led to a series of investigations of the utmost importance to both the chemist and the physicist.

In order that the significance of these investigations may be understood it may be well to summarize very briefly some of the more important properties of the X-ray.

The bombardment of metal plates, usually of platinum, by electrons gives rise to X-rays. The radiation issuing from an X-ray tube is very far from homogeneous. When screens of different materials and varying thicknesses are interposed in the path of the rays, the degree of absorption is irregular. It has been found, however, that every substance when properly stimulated is capable of emitting a homogeneous and characteristic X-radiation, the penetrating power of which is wholly determined by the nature of the elements of which the substance is composed. The penetrating power of this typical X-radiation increases with the atomic weight of the radiating element. With elements whose atomic weights are less than 24, the radiation is too feeble to be measured. It is important to note that this property of the elements is not a periodic function of the atomic weight. This type of X-radiation is entirely independent of external conditions, indicating that it is closely connected with the internal structure of the atoms from which it emanates. The rays possess the power of affecting the photographic plate and also of rendering gases through which they pass conductors of electricity.

It is estimated that the wave-length of an X-ray is about 1×10^{-8} to 1×10^{-9} cm., or about one ten-thousandth of the wave-length of sodium light. It is obvious that the spacing of the lines of a grating capable of diffracting such short waves must be of the order of magnitude of intermolecular distances. It is well known that a grating owes its power of analyzing a complex system of light waves into its component wave-trains, to the series of parallel lines which are ruled upon its surface at exactly equal intervals. When a train of waves is incident upon a grating, each line acts as a center from which a diffracted train of waves emerges.

Such a grating is relatively simple in its action since it consists of a single series of centers of diffraction lying in one plane. The power of a crystal surface to reflect X-rays, however, is due to the fact that the crystal is in reality a three-dimensional diffraction grating, the atoms or molecules of which the crystal is built up, acting as the centers of diffraction. It must be borne in mind that the reflection of X-rays is in no way dependent upon the existence of a polished surface on the outside of the crystal, but rather upon the regularly spaced atoms or molecules within the crystal. To ordinary waves of light the atomic structure is so fine grained as to behave as a continuous medium, whereas to the short X-ray waves, the crystal acts as a discontinuous structure of regularly arranged particles, each of which functions as a diffraction center.

X-Ray Spectra. By making use of the reflecting power of one of the cleavage planes of a crystal, and employing different metals as anti-cathodes in an X-ray tube, Moseley * succeeded in photographing the X-ray spectra of the characteristic radiations of a number of the elements. He showed that the X-ray spectrum of an element is extremely simple and consists of two groups of lines known as the "K" and "L" radiations. As a result of careful study of the "K" radiations of thirty-nine elements from aluminium to gold, Moseley discovered that these radiations are characterized by two well-defined lines whose vibration frequency ν is connected with the atomic number of the element N, by the simple relation

$$\nu = A\,(N - 1)^2,$$

where A is a constant. When the square roots of the frequencies of the elements are plotted as abscissæ against their atomic numbers as ordinates, the points are found to lie on a straight line as shown in Fig. 11. On the other hand, if the square roots of the frequencies are plotted against the atomic weights of the elements, the relationship is no longer rectilinear. When the elements are arranged in the order of their atomic numbers instead of in the order of their atomic weights, the irregularities † hitherto noted in connection with argon, cobalt, and tellurium entirely disappear.

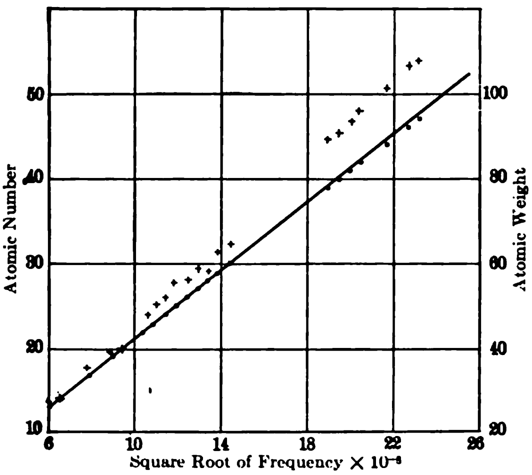


Fig. 11.

In reviewing Moseley's work on X-ray spectra, Soddy ‡ says: —

---

* Phil. Mag., 26, 210 (1913); 27, 703 (1914).

† See p. 29.

‡ Ann. Reports on the Prog. of Chemistry, p. 278 (1914).

"A veritable roll-call of the elements has been made by this method. Thirty-nine elements, with atomic weights between those of aluminium and gold, have been examined in this way, and in every case the lines of the X-ray spectrum have been found to be simply connected with the integer that represents the place assigned to it by chemists in the periodic table."

One of the most interesting results of this "roll-call" of the elements is the fixing of the number of possible rare-earth elements. Between barium and tantalum there are places for only fifteen rare-earth elements and fourteen of these places are filled. While future investigation may necessitate some rearrangement in the order of tabulation, the total number of these elements is limited to fifteen.

Periodicity among the Radio-elements. The problem of placing the newly discovered radio-elements in the periodic table remained unsolved until 1913, when Fajans* and Soddy,† working independently, discovered an important generalization concerning the changes in chemical properties resulting from the expulsion of α- and β-particles during radioactive transformation. This important generalization may be stated as follows: — *The expulsion of an α-particle causes a radioactive element to shift its position in the periodic table two places in the direction of decreasing atomic weight, whereas the emission of a β-particle causes a shift of one place in the opposite direction.* This generalization not only agrees with our present theory of atomic structure, but may be shown to be a necessary consequence of this theory.

The loss of an α-particle or helium atom involves a loss of 4 units in atomic weight and of 2 units of positive electricity from the nucleus of the atom. In consequence of this loss, the atomic number is diminished by 2 units and the resulting new element will find a place in the periodic table two groups to the left of that occupied by the parent element. On the contrary, while the expulsion of a β-particle, or electron, involves practically no change in mass, the nucleus of the parent atom suffers a loss of 1 unit of negative electricity. This loss is equivalent to a gain of 1 unit of positive electricity, or to an increase of 1 unit in the atomic number, and in consequence, the position of the new element in the periodic table will be shifted one group to the right of that occupied by the parent element.

---

* Physikal. Zeit., **14**, 49 (1913).

† Chem. News, **107**, 97 (1913).

Soddy's arrangement of all of the radio-elements in accordance with this generalization is shown in Fig. 12. Thus, starting with the element uranium in Group VIA, we may follow the successive

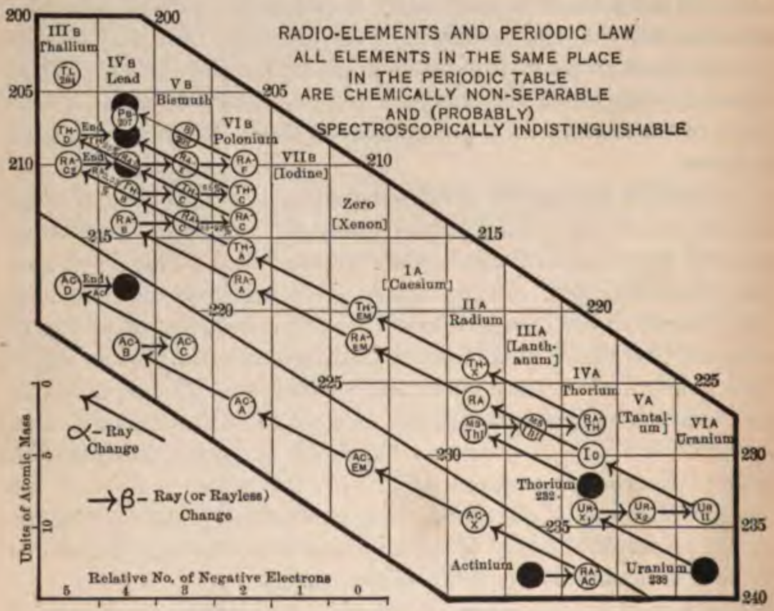


Fig. 12.

steps in the radium disintegration series which was discussed in the preceding chapter. The element UX_1 resulting from U by the loss of an α-particle is placed in Group IVA. This element in turn undergoes a β-ray change producing the element UX_2 which is accordingly placed in Group VA. The element UII in Group VIA is formed from UX_2 by β-ray disintegration, while the element Io results from the loss of an α-particle by UII with a consequent shifting of two places to the left in the table. A similar loss of an α-particle by Io brings us to the element Ra in Group

IIA. In the successive steps of this disintegration from U to Ra, three α-particles or 12 units of atomic mass are lost, and the atomic weight of Ra, as calculated from that of U, agrees with the atomic weight found by direct experiment. In like manner the remaining stages of the disintegration may be followed to the end-product in Group IVB.

Isotopes. Perhaps the most striking feature in the table is the occurrence of several different elements in the same place, as for example in Group IVB, where in the place occupied by the element Pb, we also find RaB, RaD, ThB, and AcB, together with four other elements to which no names have been assigned, but which are none the less stable end-products. The individual members of such a group of elements occupying the same place in the periodic table, and being in consequence chemically identical, are known as *isotopes*. Isotopic elements have identical arc and spark spectra and, except for differences in atomic weight, are chemically indistinguishable.

Making use of the fact that two gaseous elements having different atomic weights diffuse at different rates, Thomson and Aston have recently succeeded in separating neon into two isotopes having atomic weights 20 and 22 respectively. This is the only method which has thus far given promise of success in effecting isotopic separations.

It is interesting to note in Soddy's table (Fig. 12), that "the ten occupied spaces (groups) contain nearly forty distinct elements, whereas if chemical analysis alone had been available for their recognition, only ten elements could have been distinguished."

The Hydrogen-Helium System of Atomic Structure. A generalization similar to that just outlined for the radio-elements has been found by Harkins and Wilson* to hold true for the lighter elements which apparently do not undergo appreciable α-ray disintegration. Beginning with helium and adding 4 units of atomic weight for each increase of 2 units in the atomic number, gives the atomic weights of the elements in the even-numbered groups of the periodic table, neglecting small changes in mass due to nuclear packing. This rule has been found to hold very closely for all of the elements having atomic weights below 60.

---

* Proc. Nat. Acad., Vol. I, p. 276 (1915).

The atomic weights of the elements of the odd-numbered groups can be calculated by a similar rule, provided that the atom of lithium, the first member of the odd-numbered groups, be assumed to be made up of 1 hydrogen and 3 helium nuclei. The following table gives the results as calculated by Harkins and Wilson for the first three series of the periodic table.

The so-called theoretical atomic weights are calculated on the basis H = 1, while the experimentally determined values are on the basis O = 16 or H = 1.0078. The remarkably close agreement between the two sets of values is taken as an indication that the packing effect, resulting from the formation of the elements from hydrogen nuclei and attendant electrons, is very small. This packing effect has been estimated to involve a decrease in atomic mass of about 0.77 per cent, and is believed to be due almost entirely to the formation of the helium atom. The hydrogen-helium hypothesis of atomic structure offers a rational explanation of many interesting but hitherto obscure facts concerning the nature of the elements.

Relation between Atomic Weights and Atomic Numbers. For all elements whose atomic weights are less than that of nickel, Harkins finds the following simple mathematical relation to hold,

$$W = 2N + \tfrac{1}{2} + \tfrac{1}{2}(-1)^{N-1},$$

where W is the atomic weight and N is the atomic number. In other words, the atomic weights are a linear function of the atomic numbers.

The Periodic Law. In the light of recent discoveries the periodic law acquires new significance; in fact to-day the periodic law may be regarded as the most comprehensive generalization in the whole science of chemistry.

Attention has already been directed in an earlier chapter to the most apparent of the imperfections in Mendeléeff's system of classification of the elements. While the later tables are more complete than the original, owing in part to the discovery of new elements, it must be admitted nevertheless that relatively little real progress has been made until recently toward removing the seemingly inherent defects of the system.

THE HELIUM — H_3 SYSTEM OF ATOMIC STRUCTURE. H = 1.0078.

	0	1	2	3	4	5	6	7	8	
At. No.	2	3	4	5	6	7	8	9		
	He	Li	Be	B	C	N	O	F		
Ser. 2...	He	He + H_3	2 He + H	2He + H_3	3 He	3 He + H_2	4 He	4 He + H_3		
Theor...	4.00	7.00	9.0	11.0	12.00	14.00	16.00	19.00		
Det.....	4.00	6.94	9.1	11.0	12.00	14.01	16.00	19.00		
At. No..	10	11	12	13	14	15	16	17		
	Ne	Na	Mg	Al	Si	P	S	Cl		
Ser. 3...	5 He	5 He + H_3	6 He	6 He + H_3	7 He	7 He + H_3	8 He	8 He + H_3		
Theor...	20.0	23.0	24.00	27.0	28.0	31.00	32.00	35.00		
Det.....	20.0	23.0	24.32	27.1	28.3	31.02	32.07	35.46		
At. No..	18	19	20	21	22	23	24	25	26	27
	A	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co
Ser. 4...	10 He	9 He + H_3	10 He	11 He	12 He	12 He + H_3	13 He	13 He + H_3	14 He	14 He + H_3
Theor...	40.0	39.00	40.00	44.0	48.0	51.0	52.0	55.00	56.00	59.00
Det.....	39.9	39.10	40.07	44.1	48.1	51.0	52.0	54.93	55.84	58.97

Increment from Series 2 to Series 3 = 4 He. Increment from Series 3 to Series 4 = 5 He (4 He for K and Ca). Increment from Series 4 to Series 5 = 6 He.

A satisfactory periodic table should meet the following requirements: —

(1) It should afford a place for isotopic elements such as lead.

(2) The radio-elements together with their α- and β-disintegration products should be shown.

(3) It should contain no vacant spaces except those corresponding to the atomic numbers of undiscovered elements.

(4) It should bring out the relation between the elements constituting a main group and those forming the corresponding subgroup. For example, the relation between the elements Be, Mg, Ca, Sr, Ba, and Ra on the one hand, and the elements Zn, Cd, and Hg on the other, should be emphasized.

(5) The elements of Group O and Group VIII should fit naturally in the table.

(6) All of the foregoing conditions should be shown by means of a continuous curve connecting the elements in the order of their *atomic numbers*, the latter having been shown to be more characteristic of an element than its atomic weight.

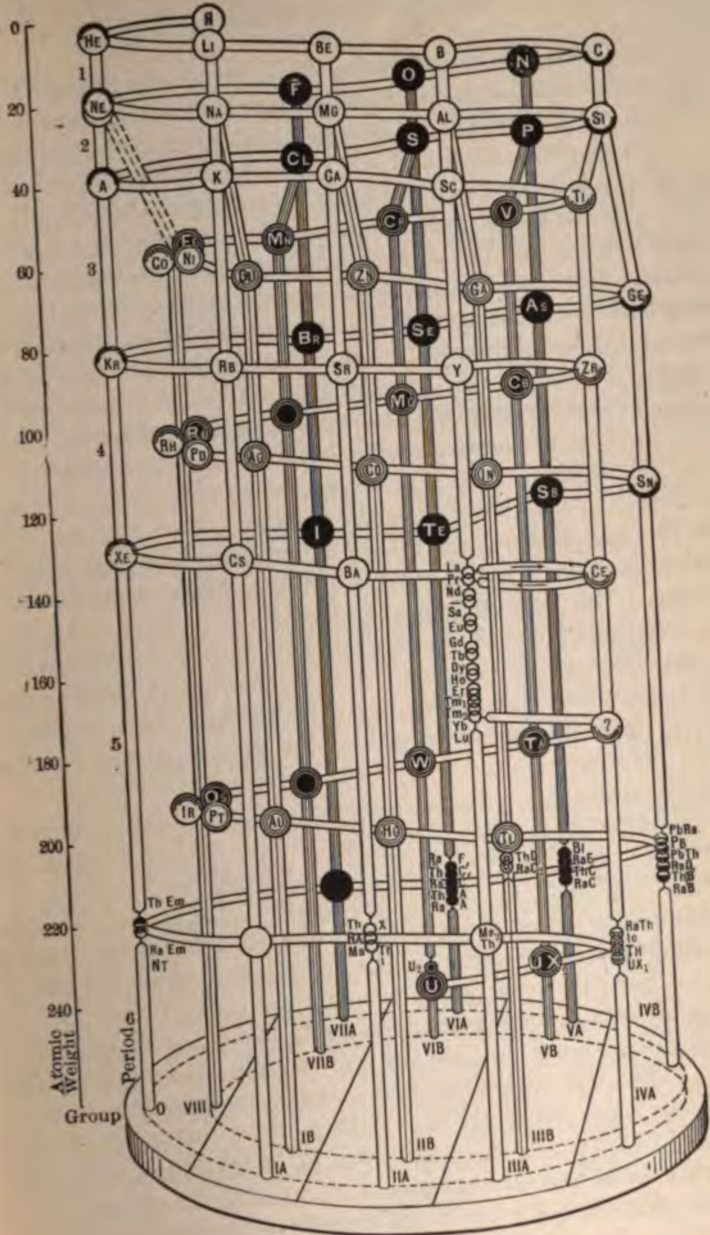
A table which satisfactorily meets these requirements has recently been devised by Harkins and Hall. This table may be constructed in the form of a helix in space or as a spiral in a plane. The following description of the helical arrangement, shown in Fig. 13, is taken verbatim from the original paper of Harkins and Hall.*

"The atomic weights are plotted from the top down, one unit of atomic weight being represented by one centimeter, so the model is about two and one-half meters high. . . .

"The balls representing the elements are supposed to be strung on vertical rods. All of the elements on one vertical rod belong to one group, have on the whole the same maximum valence, and are represented by the same *color*. The group numbers are given at the bottom of the rods. On the outer cylinder the electro-negative elements are represented by black circles at the back of the cylinder, and electro-positive elements by white circles on the front of the cylinder. The transition elements of the zero and fourth groups are represented by circles which are half black and half

---

* Jour. Am. Chem. Soc., **38**, 169 (1916).



0
20
40
60
80
100
120
140
160
180
200
220
240
Atomic Weight
Periode
1
2
3
4
5
6
Group
H
He
Li
Be
B
C
N
O
F
Ne
Na
Mg
Al
Si
P
S
Cl
A
K
Ca
Sc
Ti
V
Cr
Mn
Fe
Co
Ni
Cu
Zn
Ga
Ge
As
Se
Br
Kr
Rb
Sr
Y
Zr
Cb
Mo
Ru
Rh
Pd
Ag
Cd
In
Sn
Sb
Te
I
Xe
Cs
Ba
La
Pr
Nd
Sa
Eu
Gd
Tb
Dy
Ho
Er
Tm1
Tm2
Yb
Lu
Ce
?
Ta
W
Os
Ir
Pt
Au
Hg
Tl
ThD
RaC
Bi
RaE
ThC
RaC
PbRa
Pb
PbTh
RaD
ThB
RaB
Ra F
Th C1
Ra C1
Th A
Ra A
Th Em
Ra Em
Nt
Th X
Ra
Ms Th1
Ms Th2
RaTh
Io
Th
UX1
UX2
U2
U
0
VIII
IA
IB
IIA
IIB
IIIA
IIIB
IVA
IVB
VA
VB
VIA
VIB
VIIA
VIIB

Fig. 13.

white. The inner loop elements are intermediate in their properties. Elements on the back of the inner loop are shown as heavily shaded circles, while those on the front are shaded only slightly.

"In order to understand the table it may be well to take an imaginary journey down the helix, beginning at the top. Hydrogen (atomic number and atomic weight = 1) stands by itself, and is followed by the first inert, zero group, and zero valent element helium. Here there comes the extremely sharp break in chemical properties with the change to the strongly positive, univalent element lithium, followed by the somewhat less positive bivalent element, beryllium, and the third group element boron, with a positive valence of three, and a weaker negative valence. At the extreme right of the outer cylinder is carbon, the fourth group transition element, with a positive valence of four, and an equal negative valence, both of approximately equal strength. The first element on the back of the cylinder is more negative than positive, and has a positive valence of five, and a negative valence of three. The negative properties increase until fluorine is reached and then there is a sharp break of properties, with the change from the strongly negative, univalent element fluorine, through the zero valent transition element neon, to the strongly positive sodium. Thus in order around the outer loop the second series of elements are as follows: —

Group number......	0	1	2	3	4	5	6	7
Maximum valence...	0	1	2	3	4	5	6	7
Element...........	He	Li	Be	B	C	N	O	F
Atomic number.....	2	3	4	5	6	7	8	9

"After these comes neon, which is like helium, sodium which is like lithium, etc., to chlorine, the eighth element of the second period. For the third period the journey is continued, still on the outer loop, with argon, potassium, calcium, scandium, and then begins with titanium, to turn for the first time into the inner loop. Vanadium, chromium, and manganese, which comes next, are on the inner loop, and thus belong, not to main but to sub-groups. *This is the first appearance in the system of sub-group elements.* Just beyond manganese a catastrophe of some sort seems to take place, for here three elements of one kind, and therefore belonging to one group, are deposited. The eighth group in this table takes the place on the inner loop which the rare gases of the atmosphere fill on the outer loop. The eighth group is thus a sub-group of the zero group.

"After the eighth group elements, which have appeared for the first time, come copper, zinc, and gallium; and with germanium, a fourth group element, the helix returns to the outer loop. It then passes through arsenic, selenium, and bromine, thus completing the first long period of 18 elements. Following this there comes a second long period, exactly similar, and also containing 18 elements.

"The relations which exist may be shown by the following natural classification of the elements. They may be divided into cycles and periods as follows:

TABLE I.

Cycle 1 = 4^2 elements.

1st short period........ He — F = 8 = 2 × 2^2 elements.
2nd short period....... Ne — Cl = 8 = 2 × 2^2 elements.

Cycle 2 = 6^2 elements.

1st long period......... *A* — Br = 18 = 2 × 3^2 elements.
2nd long period........ Kr — I = 18 = 2 × 3^2 elements.

Cycle 3 = 8^2 elements.

1st very long period.... Xe — Eka-I = 32 = 2 × 4^2 elements.
2nd very long period.... Nt — U

"The last very long period, and therefore the last cycle, is incomplete. It will be seen, however, that these remarkable relations are perfect in their regularity. These are the relations, too, which exist in the completed system,* and are not like many false numerical systems which have been proposed in the past where the supposed relations were due to the counting of blanks which do not correspond to atomic numbers. This peculiar relationship is undoubtedly connected with the variations in structure of these complex elements, but their meaning will not be apparent until we know more in regard to atomic structure.

---

* If elements of atomic weights two and three are ever discovered then the zero cycle would contain 2^2 elements, and period number one should then be said to begin with lithium. Such extrapolation, however, is an uncertain basis for the prediction of such elements.

"The first cycle of two short periods is made up wholly of outer loop or main group elements. Each of the long periods of the second cycle is made up of main and of sub-group elements, and each period contains one eighth group. The only complete very long period is made up of main and of sub-group elements, contains one eighth group, and would be of the same length (18 elements) as the long periods if it were not lengthened to 32 elements by the inclusion of the rare earths.

"The first long period is introduced into the system by the insertion of iron, cobalt, and nickel, in its center, and these are three elements whose atomic numbers increase by steps of one while their valence remains constant. The first very long period is formed in a similar way by the insertion of the rare earths, another set of elements whose atomic numbers increase by one while the valence remains constant.

"In this periodic table the *maximum* valence for a group of elements may be found by beginning with *zero* for the zero group and counting toward the front for *positive* valence, and toward the back for *negative* valence.

"The negative valence runs along the spirals toward the back as follows: —

0	−1	−2	−3	−4
Ne	F	O	N	C
A	Cl	S	P	Si

"Beginning with helium the relations of the maximum theoretical valences run as follows: —

Case 1. He–F.... 0, 1, 2, 3, 4, 5, 6, 7, but does not rise to 8. Drops by 7 to 0.
Ne–Cl... 0, 1, 2, 3, 4, 5, 6, 7, but does not rise to 8. Drops by 7 to 0.
Case 2. A–Mn... 0, 1, 2, 3, 4, 5, 6, 7, 8, 8. Drops by 7 to 1.
Fe, Co, Ni
Case 1. Cu–Br
Case 2. Kr–Ru, Rh, Pd.

"In the third increase, the group number and maximum valence of the group rise to 8, three elements are formed, and the drop is again by 7 to 1.

"Thus in every case when the valence drops back the drop in maximum group valence is 7, either from 7 to 0, or from 8 to 1.

This is another illustration of the fact that the eighth group is a sub-group of the zero group. The valence of the zero group is zero. According to Abegg the contra-valence, seemingly not active in this case, is eight.

"In Fig. 13 the table is divided into *five divisions* by four straight lines across the base. These divisions contain the following groups: —

Division......	0	1	2	3	4
Groups.......	0,8	1,7	2,6	3,5	4,4

"The two groups of any division are said to be complementary. It will be seen that the sum of the group numbers in any division is equal to 8, as is also the sum of the maximum valences. The algebraic sum of the characteristic valences of two complementary groups is always zero. *In any division in which the group numbers are very different, the chemical properties of the elements of the complementary main groups are very different, but when the group numbers become the same, the chemical properties become very much alike.* Thus the greatest difference in group numbers occurs in division 8, where the difference is 8, and in the two groups there is an extreme difference in chemical properties, as there is also in division 1 between Groups 1 and 7.

"*Whenever the two main groups of a division are very different in properties, each of the sub-groups is quite different from its related main group.* Thus copper in Group IB is not very closely related to potassium Group IA in its properties, and manganese is not very similar to chlorine, but *as the group numbers approach each other the main and sub-groups become much alike.* Thus scandium is quite similar to gallium in its properties, and titanium and germanium are very closely allied to silicon.

"One important relation is that *on the outer cylinder the main groups IA, IIA, IIIA, become less positive as the group number increases, while on the inner loop the positive character increases from Group IB to IIB,* and at the bottom of the table the increase from IIB to IIIB is considerable. Thus thallium is much more positive than mercury. It has already been noted that in the case of the rare earths also the usual rule is inverted, that is the basic properties decrease as the atomic weight increases."

CHAPTER VI.

GASES.

The Gas Laws. Matter in the gaseous state possesses the property of filling completely and to a uniform density any available space. Among the most pronounced characteristics of gases are lack of definite shape or volume, low density and small viscosity. The laws expressing the behavior of gases under different conditions are relatively simple and to a large extent are independent of the nature of the gas. The temperature and pressure coefficients of all gases are very nearly the same.

In 1662, Robert Boyle discovered the familiar law that *at constant temperature, the volume of a gas is inversely proportional to the pressure upon it.* This may be expressed mathematically as follows: —

$$v \propto \frac{1}{p} \text{ (temperature constant)}$$

where v is the volume and p the pressure.

In 1801, Gay-Lussac discovered the law of the variation of the volume of a gas with temperature.

This law may be formulated thus: — *At constant pressure, the volume of a gas is directly proportional to its absolute temperature,* or

$$v \propto T \text{ (pressure constant).}$$

There are three conditions which may be varied, viz., volume, temperature and pressure. The preceding laws have dealt with the relation between two pairs of the variables when the third is held constant. There remains to consider the relation between the third pair of variables, pressure and temperature, the volume being kept constant. Evidently a necessary corollary of the first two laws is that *at constant volume, the pressure of a gas is directly proportional to its absolute temperature*, or

$$p \propto T \text{ (volume constant).}$$

is removed from
the require-
or *per-*
behavior.
equation is
the corre-

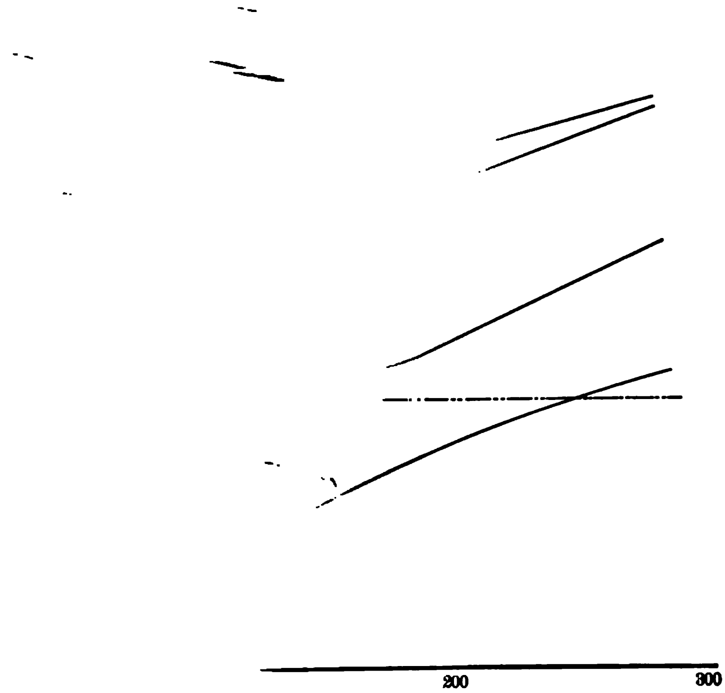


Fig. 14.

s ordinates, for an ideal gas we should
parallel to the axis of abscissæ, as shown in
obtained by Amagat with three typical
in the same diagram. It will be apparent
gases depart widely from ideal behavior. In
ogen pv increases continuously with the pressure,

value for all gases. If M is the molecular weight of the
$= R$. Equation (4) is the fundamental gas equation.

Evaluation of the Molecular Gas Constant. Since the
of p and v represents work, and T is a pure number, R
expressed in energy units. There are four different units
the molecular gas constant is commonly expressed, viz., (1
centimeters, (2) ergs, (3) calories, and (4) liter-atmospher

1. *R in gram-centimeters.* The volume, v, of 1 mol. of
0° and 76 cm. is 22.4 liters or 22,400 cc. The pressure, p, i
multiplied by 13.59, (the density of mercury), or 1033.3 gr
square centimeter. Substituting we obtain

$$R = \frac{p_0v_0}{T} = \frac{1033.3 \times 22{,}400}{273} = 84{,}760 \text{ gr. cm.}$$

2. *R in ergs.* To convert gram-centimeters into ergs
multiply by the acceleration due to gravity, $g = 980.6$
sec. per sec., or

$$R = 84{,}760 \times 980.6 = 83{,}150{,}000 \text{ ergs.}$$

3. *R in calories.* To express work in terms of heat,
divide by the mechanical equivalent of heat, or since 1 c
equivalent to 42,640 gr. cm. or 41,830,000 ergs, we have

$$R = \frac{83{,}150{,}000}{41{,}830{,}000} = 1.99 \text{ cal. (approximately 2 cal.)}$$

4. *R in liter-atmospheres.* A liter-atmosphere may be
as the work done by 1 atmosphere on a square decimeter
a decimeter. If p_0 is the pressure in atmospheres, and
volume in liters, we have

$$R = \frac{p_0v_0}{T} = \frac{22.4}{273} = 0.0821 \text{ liter-atmosphere.}$$

Deviations from the Gas Laws. Careful experim
Amagat * and others on the behavior of [illegible]
of temperature and pressure [illegible]
gas equation, $pv = RT$, is not tri
the deviations depending
conditions under which it
the gas laws are more nea

---

* Ann. Chi

higher the temperature and the further the gas is removed from the critical state. A gas which would conform to the requirements of the fundamental gas equation is called an *ideal* or *perfect gas*. Almost all gases are far from ideal in their behavior. At constant temperature the product, pv, in the gas equation is constant, so that if we plot pressures as abscissæ and the corre-

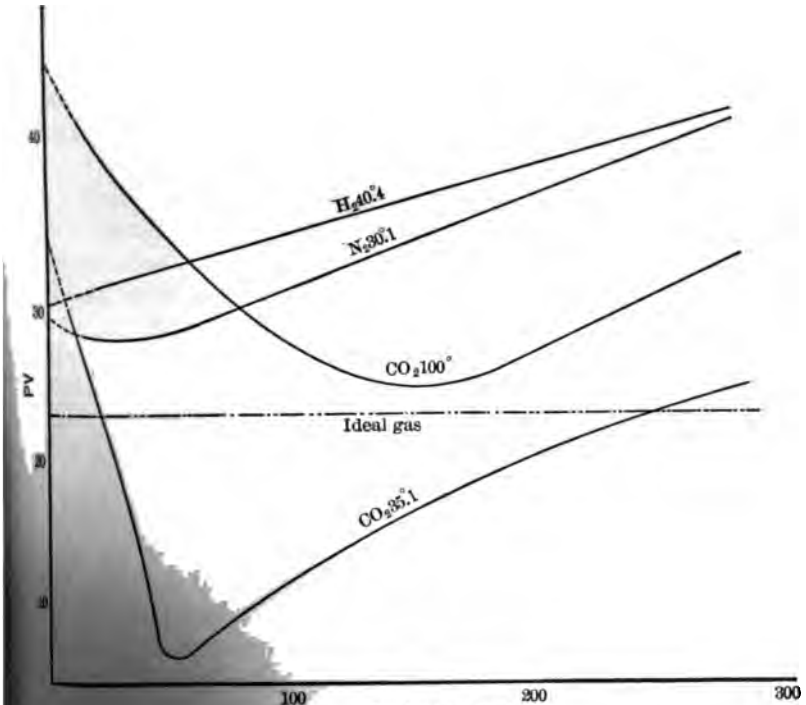


Fig. 14.

sponding values of pv as ordinates, for an ideal gas we should
ight line parall to the axis of abscissæ, as shown in
ults obt d by Amagat with three typical
me diagram. It will be apparent
t widely from ideal behavior. In
eases continuously with the pressure,

while with nitrogen and carbon dioxide it first decreases, attains to a minimum value and beyond that point increases with increasing pressure. With the exception of hydrogen, all gases show a minimum in the curve, thus indicating that at first the compressibility is greater than corresponds with the law of Boyle, but diminishes continuously until, for a short range of pressure, the law is followed strictly: beyond this point the compressibility is less than Boyle's law requires.

Hydrogen is exceptional in that it is always less compressible than the law demands. This is true for all ordinary temperatures, but it is highly probable that at extremely low temperatures the curve would show a minimum. The two curves for carbon dioxide at 31°.5 and 100° illustrate the fact that the deviations from the gas laws become less as the temperature increases. The deviations of gases from the laws of Boyle and Gay-Lussac, as well as their behavior in general, may be satisfactorily accounted for on the basis of the kinetic theory.

Kinetic Theory of Gases. The first attempt to explain the properties of gases on a purely mechanical basis was made by Bernoulli in 1738. Subsequently, through the labors of Kroenig, Clausius, Maxwell, Boltzmann and others, his ideas were developed into what is known today as the kinetic theory of gases. According to this theory, gases are considered to be made up of minute, perfectly elastic particles which are ceaselessly moving about with high velocities, colliding with each other and with the walls of the containing vessel. These particles are identical with the molecules defined by Avogadro. The volume actually occupied by the gas molecules is supposed to be much smaller than the volume filled by them under ordinary conditions, thus allowing the molecules to move about free from one another's influence except when they collide. The distance through which a molecule moves before colliding with another molecule is known as its *mean free path*. In terms of this theory, the pressure exerted by a gas is due to the combined effect of the impacts of the moving molecules upon the walls of the containing vessel, the magnitude of the pressure being dependent upon the kinetic energy of the molecules and their number.

Derivation of the Kinetic Equation. Starting with the assumptions already made, it is possible to derive a formula by means of which the gas laws may be deduced. Imagine n molecules, each having a mass, m, confined within the cubical vessel shown in Fig. 15, the edge of which has a length, l. While the different molecules are doubtless moving with different velocities, there must be an average velocity for all of them. Let c denote this mean velocity of translation. The molecules will impinge upon the walls in all directions but the velocity of each may be resolved according to the well-known dynamical principle into three components, x, y and z, parallel to the three rectangular axes, X, Y and Z. The analytical expression for the velocity of a single molecule, M, is

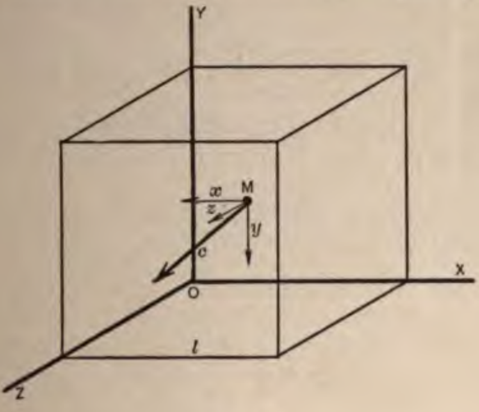


Fig. 15.

$$c^2 = x^2 + y^2 + z^2.$$

In words, this means that the effect of the collision of the molecule upon the wall of the containing vessel, is equivalent to the combined effect of successive collisions of the molecule perpendicular to the three walls of the cubical vessel with the velocities x, y and z respectively. Fixing our attention upon the horizontal component, the molecule will collide with the wall with a velocity x, and owing to its perfect elasticity it will rebound with a velocity

$-x$, having suffered no loss in kinetic energy. The momentum before collision was mx and after collision it will be $-mx$, the total change in momentum being $2\,mx$. The distance between the two walls being l, the number of collisions on a wall in unit time will be, x/l, and the total effect of a single molecule in one direction in unit time will be $2\,mx \cdot x/l = 2\,mx^2/l$. The same reasoning is applicable to the other components, so that the combined action of a single molecule on the six sides of the vessel will be

$$\frac{2\,m}{l}(x^2 + y^2 + z^2) = \frac{2\,mc^2}{l}.$$

There being n molecules, the total effect will be $\frac{2\,mnc^2}{l}$. The entire inner surface of the cubical vessel being $6\,l^2$, the pressure p, on unit area, will be

$$p = \frac{2\,mnc^2}{6l^3} = \frac{1}{3} \cdot \frac{mnc^2}{l^3};$$

but since l^3 is the volume of the cube, which we will denote by v, we have

$$p = \frac{1}{3} \cdot \frac{mnc^2}{v},$$

or

$$pv = \frac{1}{3} \cdot mnc^2.$$

This is the fundamental equation of the kinetic theory of gases. While the equation has been derived for a cubical vessel, it is equally applicable to a vessel of any shape whatever, since the total volume may be considered to be made up of a large number of infinitesimally small cubes, for each of which the equation holds.

Deductions from the Kinetic Equation. *Law of Boyle.* In the fundamental kinetic equation, $pv = \frac{1}{3}\,mnc^2$, the right-hand side is composed of factors which are constant at constant temperature, and therefore the product, pv, must be constant also under similar conditions. This is clearly Boyle's law.

Law of Gay-Lussac. The kinetic equation may be written in the form

$$pv = \frac{2}{3} \cdot \frac{1}{2} mnc^2.$$

The kinetic energy of a single molecule being represented by $1/2\ mc^2$, the total kinetic energy of the molecules of the gas will be $1/2\ mnc^2$. *Therefore the product of the pressure and volume of the gas is equivalent to two-thirds of the kinetic energy of its molecules.* A corollary to this proposition is that *at constant pressure, the average kinetic energy of the molecules in equal volumes of different gases is the same.* The law of Gay-Lussac teaches that at constant volume, the pressure of a gas is directly proportional to its absolute temperature. Taking this together with the fact that the pressure of a gas at constant volume is directly proportional to the mean kinetic energy of its molecules, it follows that *the mean kinetic energy of the molecules of a gas is directly proportional to its absolute temperature.* Thus we see that the absolute temperature of a gas is a measure of the mean kinetic energy of its molecules. This deduction is partially based upon the experimentally-determined law of Gay-Lussac. Having obtained a definiton of temperature in terms of kinetic energy, it is easy to derive Gay-Lussac's law from the fundamental kinetic equation. Writing the equation in the form

$$pv = \frac{2}{3} \cdot \frac{1}{2} mnc^2,$$

it is apparent that pv is directly proportional to the total kinetic energy of the gas molecules, or in other words, is directly proportional to its absolute temperature, which is the most general statement of Gay-Lussac's law.

Hypothesis of Avogadro. If equal volumes of two different gases are measured under the same pressure, we will have

$$pv = 1/3\ n_1m_1c_1^2 = 1/3\ n_2m_2c_2^2, \qquad (1)$$

where n_1 and n_2, m_1 and m_2, and c_1 and c_2 denote the number, mass and velocity of the molecules in the two gases. If the gases are measured at the same temperature, the molecules of each possess the same mean kinetic energy, or

$$1/2\, m_1 c_1^2 = 1/2\, m_2 c_2^2. \qquad (2)$$

Dividing equation (1) by equation (2), we have

$$n_1 = n_2,$$

or under the same conditions of temperature and pressure equal volumes of the two gases contain the same number of molecules. This is the hypothesis of Avogadro.

Law of Graham. If the fundamental kinetic equation be solved for c, we have

$$c = \sqrt{\frac{3\,pv}{mn}};$$

but $v/mn = 1/d$, where d is the density of the gas, and therefore we may write

$$c = \sqrt{\frac{3\,p}{d}}.$$

If the pressure remains constant it is evident that the mean velocities of the molecules of two gases are inversely proportional to the square roots of their densities, a law which was first enunciated by Graham in 1833 as the result of his experiments on gaseous diffusion.

Mean Velocity of Translation of a Gaseous Molecule. By substituting appropriate values for the various magnitudes in the equation

$$c = \sqrt{\frac{3\,pv}{mn}},$$

it is possible to calculate the mean velocity of the molecules of any gas. Thus, for the gram-molecule of hydrogen at 0° and 76 cm. pressure, $p = 76 \times 13.59 = 1033.3$ gr. per sq. cm. $= 1033.3 \times 980.6$ dynes per sq. cm., $v = 22{,}400$ cc., and $mn = 2.016$ gr.

Substituting these values in the above equation we have,

$$c = \sqrt{\frac{3 \times 1033.3 \times 980.6 \times 22{,}400}{2.016}} = 183{,}780 \text{ cm. per sec.}$$

Thus at 0° the molecule of hydrogen moves with a speed slightly greater than one mile per second. This enormous speed is only attained along the mean free path, the frequent collisions with other molecules rendering the actual speed much less than that calculated.

Equation of van der Waals. As has been pointed out in a previous paragraph, the gas laws are merely limiting laws and while they hold quite well up to pressures of about 2 atmospheres, above this pressure the differences between the observed and calculated values become steadily larger. In the case of hydrogen, Natterer was the first to show that the product of pressure and volume is invariably higher than it should be. A possible explanation of this departure from the gas laws was offered by Budde, who proposed that the volume, v, in the equation $pv = RT$, should be corrected for the volume occupied by the molecules themselves. If this volume correction be denoted by b, then the gas equation becomes

$$p(v-b) = RT,$$

where b is a constant for each gas. Budde calculated the value of b for hydrogen and found it to remain constant for pressures varying from 1000 to 2800 meters of mercury.

While Budde's modification of the gas equation is quite satisfactory in the case of hydrogen, it fails when applied to other gases. In general, the compressibility at low pressures is considerably greater than can be accounted for by Boyle's law. The compressibility reaches a minimum value, and then increases rapidly so that pv passes through the value required by the law. This suggests that there is some other correction to be applied in addition to the volume correction introduced into the gas equation by Budde. van der Waals pointed out in 1879, that in the deduction of Boyle's law by means of the fundamental kinetic equation, the tacit assumption is made that the molecules exert no mutual attraction. While this assumption is undoubtedly justifiable when the gas is subjected to a very low pressure, it no longer remains so when the gas is strongly compressed. A little consideration will make it apparent that when increased pressure is applied to a gas, the resulting volume will become less than that calculated, owing to molecular attraction. In other words the molecular attraction and the applied pressure act in the same direction and the gas behaves as if it were subjected to a pressure greater than that actually applied. Van der Waals showed that this correction is inversely proportional to the square of the volume, and since it augments the applied pressure the expression $p + a/v^2$ is substituted for p in the gas equation, a being the constant of molecular attraction. The corrected equation then becomes

$$(p + a/v^2)\,(v - b) = RT.$$

This is known as the equation of van der Waals. It is applicable not only to strongly compressed gases, but also to liquids as well. While it will be given detailed consideration in a subsequent chapter, it may be of interest to point out at this time the satisfactory explanation which it offers of the experimental results of Amagat, to which we have already made reference, (page 72). When v is large, both b and a/v^2 become negligible, and van der Waals' equation reduces to the simple gas equation, $pv = RT$. We may predict, therefore, that any influence tending to increase v will cause the gas to approach more nearly to the ideal condition. This is in accord with the results of Amagat's experiments, which show that an increase of temperature at constant pressure, or a diminution of pressure at constant temperature, causes the gas to tend to follow the simple gas laws. The equation also offers a satisfactory explanation of the exceptional behavior of hydrogen when it is subjected to pressure. As we have seen, pv for all gases, except hydrogen, diminishes at first with increasing pressure, reaches a minimum value, and then increases regularly. Since the volume correction in van der Waals' equation acts in opposition to the attraction correction, it is apparent that at low pressures the effect of attraction preponderates, while at high pressures the volume correction is relatively of more importance. At some intermediate pressure the two corrections counterbalance each other, and it is at this point that the gas follows Boyle's law strictly. The exceptional behavior of hydrogen may be accounted for by making the very plausible assumption that the attraction correction is negligible at all pressures in comparison with the volume correction.

Vapor Density and Molecular Weight. As has been pointed out in an earlier chapter, when a substance can be obtained in the gaseous state, the determination of its molecular weight resolves itself into finding the mass of that volume of vapor which will occupy 22.4 liters at 0° and 76 cm. It is inconvenient to weigh a volume of gas or vapor under standard conditions of temperature and pressure, but by means of the gas laws the determination made at any temperature and under any pressure can be reduced to standard conditions. For example, suppose v cc. of gas are found to weigh w grams at $t°$ and p cm. pressure, then the weight in grams of 22.4 liters or 22,400 cc. at 0° and 76 cm. will be given by the following proportion, in which M denotes the molecular weight of the substance: —

$$w : \frac{pv}{t + 273} = M : \frac{76 \times 22{,}400}{273},$$

or

$$M = \frac{w \times 76 \times 22{,}400 \times (t + 273)}{273\, pv}.$$

The determination of vapor density may be effected in either of two ways; (1) we may determine the mass of a known volume of vapor under definite conditions of temperature and pressure, or (2) we may determine the volume of a known mass under definite conditions of temperature and pressure. There are a variety of methods for the determination of vapor density; but for our purpose it will be necessary to describe but two of them. In the method of Regnault the mass of a definite volume of vapor is determined, while in the method due to Victor Meyer we measure the volume of a known mass.

Method of Regnault. In this method which is especially adapted to permanent gases, use is made of two spherical glass bulbs (Fig. 16) of approximately the same capacity, each bulb being provided with a well-ground stop-cock. By means of an airpump one bulb in evacuated as completely as possible, and is then filled, at definite temperature and pressure, with the gas whose density is to be determined. The stop-cock is then closed and the bulb weighed, the second bulb being used as a counterpoise. The use of the second bulb is largely to avoid the troublesome corrections for air displacement and for moisture, each bulb being affected in the same way and to nearly the same extent. The volume of the bulb may be obtained by weighing it first evacuated, and then filled with distilled water at known temperature. From these results we may calculate the mass per unit of volume; or we may substitute the values of w, v, p and t in the above formula and calculate M, the molecular weight. This method was used by Morley * in his epoch-making research on the densities of hydrogen and oxygen.

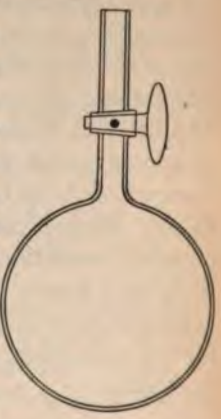


Fig. 16.

Method of Victor Meyer. In the method of Victor Meyer, a weighed amount of the substance is vaporized, and the volume which it would have occupied at the temperature of the room and under existing barometric pressure is determined. The apparatus of Meyer, shown in Fig. 17, consists of an inner glass tube A, about 1 cm. in diameter and 75 cm. in length. This tube is expanded into a bulb at the lower end, while at the top it is slightly enlarged and is furnished with two side tubes C and E. The tube A is suspended inside a heating jacket B, containing some liquid the boiling point of which is about 20° higher than the vaporizing temperature of the substance whose vapor density is to be determined. The side tube E dips beneath the surface of water in a pneumatic trough G, and serves to convey the air displaced from A to the eudiometer F. By means of the side tube C, and the glass-rod D, the small bulb containing the substance can be dropped to the bottom of A. To carry out a determination of vapor density with this apparatus, the liquid in B is heated to boiling and the sealed bulb V, containing a weighed amount of the substance, is placed in position on the rod D, the corks being tightly inserted.

---

* Smithsonian Contributions to Knowledge, (1895).

When bubbles of air cease to issue from E in the pneumatic trough, showing that the temperature within A is constant, the eudiometer F, full of water, is placed over the mouth of E, and the bulb V is allowed to drop by drawing aside the rod D. Air bubbles immediately begin to issue from E and to collect in the eudiometer. When the air ceases to collect, the eudiometer is closed by the thumb and is removed to a large cylinder of water where it is allowed to stand long enough to acquire the temperature of the room. It is then raised or lowered until the level of water inside and outside is the same, when the volume of air is carefully read off. In this method, the substance on vaporizing displaces an equal volume of air which is collected and measured, this observed volume being

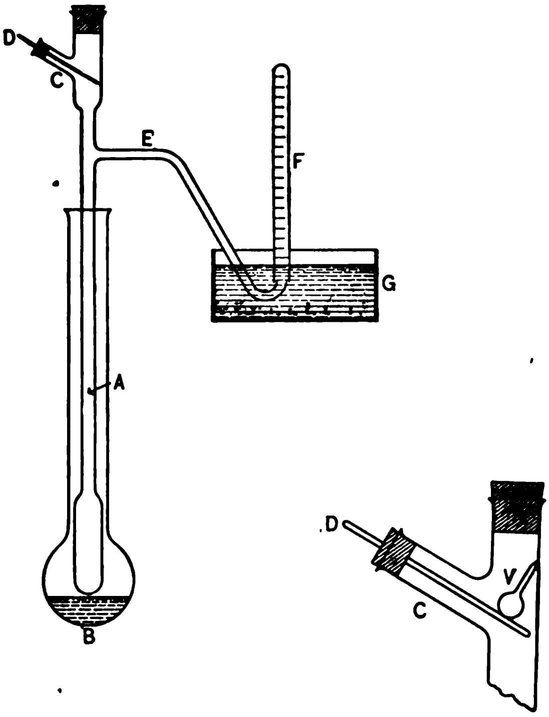


Fig. 17.

that which the vapor would occupy after reduction to the conditions under which the air is measured. It is evident that in this method we do not require a knowledge of the temperature at which the substance vaporizes. Since the air is measured over water, the pressure to which it is subjected is that of the atmosphere diminished by the vapor pressure of water at the temperature of the experiment. The method of calculating molecular weights from the observations recorded may be illustrated by the following example: — 0.1 gram of benzene (C_6H_6) was weighed out, and when vaporized, 32 cc. of air were collected over water at 17° and 750 mm. pressure. The vapor pressure of water at 17° is 14.4 mm., and the actual pressure exerted by the gas is $750 - 14.4 = 735.6$ mm. Substituting in the proportion

$$w : \frac{pv}{t + 273} = M : \frac{760 \times 22{,}400}{273},$$

and solving for M we have

$$M = \frac{0.1 \times 760 \times 22{,}400 \times (17 + 273)}{273 \times 735.6 \times 32} = 76.8.$$

The result agrees fairly well with the molecular weight of benzene (78.05) calculated from the formula.

Unless a vapor follows the gas laws very closely, the value of the molecular weight obtained by the method of Victor Meyer will be only approximate, but this approximate value will be sufficiently near to the true molecular weight to enable us to choose between the simple formula weight, given by chemical analysis, and some multiple of it.

Results of Vapor-Density Determinations. As the result of numerous vapor-density determinations extending over a wide range of temperatures, much important data has been collected concerning the number of atoms contained in the molecules of a large number of chemical compounds. The molecular weights of most of the elementary gases are double their atomic weights, showing that their molecules are diatomic. In like manner the molecular weights of mercury, zinc, cadmium and, in fact, all of the vaporizable metallic elements have been found to be identical with their atomic weights. The molecules of sulphur, arsenic, phosphorus and iodine are polyatomic, if they are not heated to too high a temperature. The investigations of Meyer and others have shown that the vapor densities of a large number of substances diminish as the temperature is increased. In other words as the temperature is raised the number of atoms contained in the molecules decreases. The molecular weight of sulphur, calculated from its vapor density at temperatures below 500°, corresponds to the formula S_8. If the vapor of sulphur is heated to 1100°, the molecular weight corresponds to the formula S_2. In fact, sulphur in the form of vapor may be represented by the formulas S_8, S_4, S_2, or even S according to the temperature at which its vapor density is determined. Iodine behaves similarly, the molecules being diatomic between 200° and 600°, while at temperatures above 1400° the vapor density has about one-half its value at the lower temperature, showing a complete breaking down of the diatomic molecules into single atoms. Heating to yet higher temperatures has failed to reveal any further decomposition. This phenomenon is not confined to the molecules of the elements alone, but is also met with in the case of the molecules of chemical compounds. The vapor density of arsenious oxide between 500° and 700° corresponds to the formula As_4O_6. As the temperature is raised, the vapor density becomes steadily smaller until, at 1800°, the calculated molecular weight corresponds to the formula As_2O_3. In like manner ferric and aluminium chlorides have been shown to have molecular weights at low temperatures corresponding to the formulas, Fe_2Cl_6 and Al_2Cl_6. The commonly-used formulas, $FeCl_3$ and $AlCl_3$, represent their molecular weights at high temperatures only. The experimental difficulties attending vapor density determinations increase as the temperature is raised, owing chiefly to the deformation of the apparatus when the material of which it is constructed approaches its melting point. Glass which can be used at relatively low temperatures only, has been replaced by specially resistant varieties of porcelain which may be used up to temperatures of 1500° or 1600°. Platinum vessels retain their shape up to temperatures between 1700° and 1800°. Measurements up to 2000° have recently been effected by Nernst and his pupils.* In their experiments use was made of a vessel of iridium, the inside and outside of which was surrounded with a cement of magnesia and magnesium chloride, the entire apparatus being heated electrically. With this apparatus they showed that the molecular weight of sulphur between 1800° and 2000° is 48, indicating that the diatomic molecule is approximately 50 per cent broken down into single atoms.

---

* Wartenberg. Zeit. anorg. Chem., 56, 320 (1907).

Abnormal Vapor Densities. In all of the cases cited above the molecular weight calculated from the vapor density corresponds either with the simple formula weight, as determined by chemical analysis, or with a multiple thereof. In no case is there any evidence of a breaking down of the simple molecule into its constituents. Substances are known, however, the molecular weights of which, calculated from their vapor densities, are less than the sum of the atomic weights of their constituents. For example, the vapor density of ammonium chloride was found to be 0.89, while that corresponding to the formula NH_4Cl should be 1.89. Similar results have been obtained with phosphorus pentachloride, nitrogen peroxide, chloral hydrate and numerous other substances. The phenomenon can be explained in either of the two following ways: (1) that the molecule has undergone a complete disruption, or (2) that the substance does not follow the law of Avogadro. Until the former explanation was shown to be correct, the latter was accepted and for a time the law of Avogadro fell into disrepute. In 1857, Deville showed that numerous chemical compounds are broken down or "dissociated" at high temperatures. Shortly afterward Kopp suggested that the abnormal vapor densities of such substances as ammonium chloride, phosphorus pentachloride, etc., might be due to thermal dissociation. If ammonium chloride underwent complete dissociation, one molecule of the salt would yield one molecule of ammonia and one molecule of hydrochloric acid gas, and the vapor density of the resulting mixture would be one-half of that of the undissociated substance, a deduction in complete agreement with the results of experiment. It remained to prove that the products of this supposed dissociation were actually present.

The first to offer an experimental demonstration of the simultaneous formation of ammonia and hydrochloric acid, when ammonium chloride is heated, was Pebal.* The apparatus which he devised for this purpose is shown in Fig. 18. It consisted of two tubes, *T* and *t*, the latter being placed within the former as indicated in the sketch. Near the top of the inner tube, which was drawn down to a smaller diameter, was a porous plug of asbestos, *C*, upon which was placed a little ammonium chloride. A stream of dry hydrogen was passed through the apparatus by means of the tubes *A* and *B*, the former entering the outer tube and the latter the inner tube. The entire apparatus was heated to a temperature above that necessary to vaporize the ammonium chloride. If the salt undergoes dissociation into ammonia and hydrochloric acid, the former being less dense than the latter, would diffuse more rapidly through the plug *C* and the vapor below the plug would

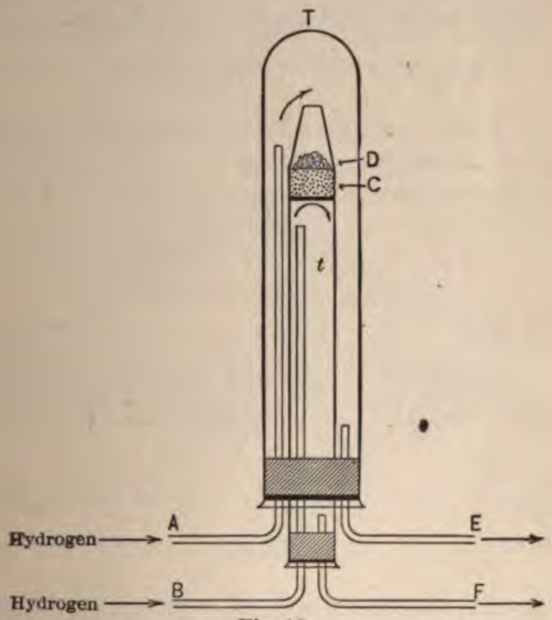


Fig. 18.

---

* Lieb. Ann., 123, 199 (1862).

be relatively richer in ammonia than the vapor above it. The current of hydrogen through *B* would therefore sweep out from the lower part of *t* an excess of ammonia, while the current through *A* would carry out from *T* an excess of hydrochloric acid. By holding strips of moistened litmus paper in the currents of gas issuing from *E* and *F*, it was possible for Pebal to test the correctness of Kopp's idea. He found that the gas issuing from *E* had an acid reaction while that escaping from *F* had an alkaline reaction. It would at first sight appear that Pebal had demonstrated beyond question that ammonium chloride undergoes dissociation into ammonia and hydrochloric acid.

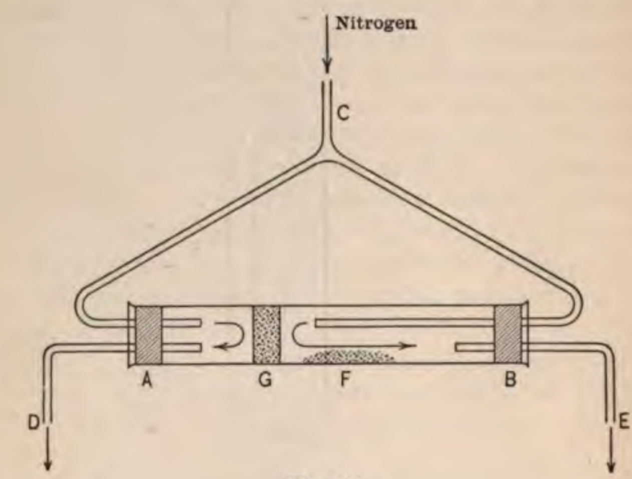


Fig. 19.

It was pointed out, however, that Pebal had heated the ammonium chloride in contact with a foreign substance, asbestos, and that this might have acted as a catalyst, promoting the decomposition into ammonia and hydrochloric acid. This objection was removed by the ingenious experiment of Than.* He devised a modification of Pebal's apparatus, as shown in Fig. 19. In the horizontal tube, *AB*, the ammonium chloride was placed at *F* and a porous plug of compressed ammonium chloride was introduced at *G*. The tube was heated and nitrogen passed in at *C*. The reactions of the currents of gas issuing at *D* and *E* were tested with litmus as in Pebal's experiment and it was found that the gas escaping from *D* was alkaline, while that issuing from *E* was acid. This experiment proved beyond question that the vapor of ammonium chloride is thermally dissociated into ammonia and hydrochloric acid. Experiments on other substances whose vapor densities are abnormally small show that a similar explanation is applicable, and thus furnish a confirmation of the law of Avogadro.

---

* Lieb. Ann., 131, 129 (1864).

Calculation of the Degree of Dissociation. Since the density of a dissociating vapor decreases with increase in temperature, it is important to be able to calculate the degree of dissocation at any one temperature. This is clearly equivalent to ascertaining the extent to which the reaction

$$NH_4Cl \rightleftarrows NH_3 + HCl$$

has proceeded from left to right. This can be determined easily from the relation of vapor density to dissociation. If we start with one molecule of gas and let α represent the percentage dissociation, then $1 - \alpha$ will denote the percentage remaining undissociated. If one molecule of gas yields n molecules of gaseous products, the total number of molecules present at any time will be

$$(1 - \alpha) + n\alpha = 1 + (n - 1)\alpha.$$

The ratio $1 : 1 + (n - 1)\alpha$ will be the same as the ratio of the density d_2 of the dissociated gas to its density in the undissociated state d_1, or

$$1 : 1 + (n - 1)\alpha = d_2 : d_1;$$

solving this proportion for α, we have

$$\alpha = \frac{d_1 - d_2}{(n - 1)d_2}.$$

The vapor density of nitrogen peroxide has been measured by E. and L. Natanson,* and the degree of dissociation at the different temperatures calculated by means of the preceding formula. The following table gives their results.

---

* Wied. Ann., **24**, 454 (1885); **27**, 606 (1886).

The course of the dissociation is shown in the accompanying illustration, Fig. 20, in which the abscissæ represent temperature and the ordinates, percentage dissociation. It will be observed

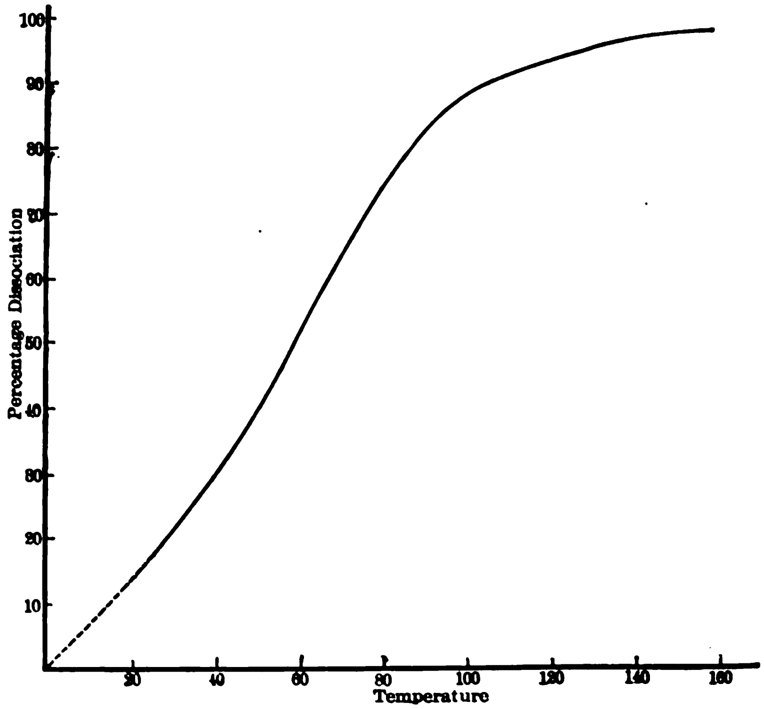


Fig. 20.

that the dissociation of nitrogen peroxide is at first nearly proportional to the temperature. It then increases more rapidly until, when about four-fifths of the molecules of N_2O_4 are broken down, the dissociation proceeds slowly to completion.

Specific Heat. The addition of heat energy to a body causes its temperature to rise. The ratio of the amount of heat supplied to the resulting rise in temperature is called the *heat capacity* of the body; obviously its value is dependent upon the initial temper-

DISSOCIATION OF NITROGEN PEROXIDE, N_2O_4.

ATMOSPHERIC PRESSURE.

(Density of $N_2O_4=3.18$; of $NO_2+NO_2=1.59$; of air $=1.00$)

Temperature. (degrees)	Density of Gas.	Percentage Dissociation.
26.7	2.65	19.96
35.4	2.53	25.65
39.8	2.46	29.23
49.6	2.27	40.04
60.2	2.08	52.84
70.0	1.92	65.57
80.6	1.80	76.61
90.0	1.72	84.83
100.1	1.68	89.23
111.3	1.65	92.67
121.5	1.62	96.23
135.0	1.60	98.69
154.0	1.58	100.00

re of the body. The *specific heat* of a substance may be defined *the heat capacity of unit mass of the substance.* If dt represents increment of temperature due to the addition of dQ units of t energy to m grams of any substance, then its specific heat, c, l be given by the equation

$$c=\frac{1}{m}\cdot\frac{dQ}{dt}.$$

pecific Heat at Constant Pressure and Constant Volume. It well known that the specific heat of a gas depends upon the ditions under which it is determined. If a definite mass of is heated under constant pressure, the value of the specific t, c_p, is different from the value of the specific heat, c_v, obned when the pressure varies and the volume remains connt. The value of c_p is invariably greater than that of c_v. en heat is supplied to a gas at constant pressure not only does temperature rise, but it also expands, and thus does external k. On the other hand, if the gas be heated in such a way that volume cannot change, none of the heat supplied will be used doing external work, and consequently its heat capacity will be less than when it is heated under constant pressure. The recognition by Mayer in 1841 of the cause of this difference between the two specific heats of a gas led him to his celebrated calculation of the mechanical equivalent of heat, and the enunciation of the first law of thermodynamics. Mayer observed that the difference between the quantity of heat necessary to raise the temperature of 1 gram of air 1° C. at constant pressure, and at constant volume respectively, was 0.0692 calorie, or

$$c_p - c_v = 0.0692 \text{ cal.}$$

That is to say, 0.0692 calorie is the amount of heat energy which is equivalent to the work required to expand 1 gram of air 1/273 of its volume at 0°. Imagine 1 gram of air at 0° enclosed within a cylinder having a cross-section of one square centimeter, and furnished with a movable, frictionless piston. Since 1 gram of air under standard conditions of temperature and pressure occupies 773.3 cc., the distance between the piston and the bottom of the cylinder will be 773.3 cm. If the temperature be raised from 0° to 1°, the piston will rise $1/273 \times 773.3 = 2.83$ cm., and since the pressure of the atmosphere is 1033.3 grams per square centimeter, the external work done by the expanding gas will be

$$1033.3 \times 2.83 = 2924.3 \text{ gr. cm.}$$

This is evidently equivalent to 0.0692 calorie and therefore, the equivalent of 1 calorie in mechanical units, J, will be

$$J = \frac{2924.3}{0.0692} = 42{,}258 \text{ gr. cm.},$$

a value agreeing very well with the best recent determinations of the mechanical equivalent of heat.

The difference between the two specific heats may be easily calculated in calories from the fundamental gas equation. Starting with 1 mol. of gas, and remembering that when a gas expands at constant pressure, the product of pressure and change in volume is a measure of the work done, we have, at temperature $T_1°$,

$$pv_1 = RT_1,$$

where v_1 is the molecular volume. Raising the temperature to

$T_2°$, the corresponding molecular volume being v_2, we have for the work done during expansion

$$p\,(v_2 - v_1) = R\,(T_2 - T_1).$$

If $T_2 - T_1 = 1°$, then the equation reduces to

$$p\,(v_2 - v_1) = R.$$

Since the difference between the molecular heats * at constant pressure and constant volume is equivalent to the external work involved when the temperature of 1 mol. of gas is raised 1°, we have

$$M\,(c_p - c_v) = p\,(v_2 - v_1),$$

where M is the molecular weight of the gas; and therefore

$$M\,(c_p - c_v) = R = 2 \text{ calories}.$$

In words, the difference of the molecular heats of any gas at constant pressure and at constant volume is 2 calories. The specific heat of a gas at constant pressure can be readily determined, by passing a definite volume of the gas, heated under constant pressure to a known temperature, through the worm of a calorimeter at such a rate that a constant difference is maintained between the temperature of the entering and the temperature of the escaping gas. Thus the number of calories which causes a definite thermal change in a certain volume of the gas is determined, and from this it is an easy matter to calculate the specific heat, c_p. The molecular heat at constant pressure for all gases approaches the limiting value, 6.5, at the absolute zero. This relation, due to Le Chatelier, may be expressed thus,

$$Mc_p = 6.5 + aT,$$

where a is a constant for each gas. The value of a for hydrogen, oxygen, nitrogen and carbon monoxide is 0.001, for ammonia, 0.0071 and for carbon dioxide, 0.0084. As the complexity of the gas increases the value of a becomes numerically greater.

The experimental determination of the specific heat of a gas at constant volume is difficult and the results obtained are not trustworthy. The chief cause of the inaccuracy of the results

---

* *The molecular heat of a gas is equal to the product of its specific heat and its molecular weight.*

is that the vessel containing the gas absorbs so much more heat than the gas itself that the correction is many times larger than the quantity to be measured. The specific heat at constant volume is almost always obtained by indirect methods, as for example by means of the preceding formula

$$M\ (c_p - c_v) = R = 2 \text{ cal.},$$

in which the values of M and c_p are known.

The molecular heats of some of the commoner gases and vapors are given in the subjoined table together with the ratio c_p/c_v.

MOLECULAR SPECIFIC HEATS.

Gas.	Mc_p	Mc_v	$c_p/c_v = \gamma$
Argon	....	....	1.66
Helium	....	....	1.66
Mercury	....	....	1.66
Hydrogen	6.88	4.88	1.41
Oxygen	6.96	4.96	1.40
Nitrogen	6.93	4.93	1.41
Chlorine	8.58	6.58	1.30
Bromine	8.88	6.88	1.29
Nitric oxide	6.95	4.95	1.40
Carbon monoxide	6.86	4.86	1.41
Hydrochloric acid	6.68	4.68	1.43
Carbon dioxide	9.55	7.55	1.26
Nitrous oxide	9.94	7.94	1.25
Water	8.65	6.65	1.28
Sulphur dioxide	9.88	7.88	1.25
Ozone	....	....	1.29
Ether	35.51	33.51	1.06

The Ratio of the Two Specific Heats. There are two methods by which the ratio c_p/c_v can be determined directly, one due to Clement and Desormes * and the other due to Kundt.†

Method of Clement and Desormes. The apparatus devised by these investigators consists, as is shown in Fig. 21, of a glass balloon flask, A, of about 20 liters capacity, furnished with two stop-cocks, D and E, and a manometer, C. The stop-cock D has an aperture nearly as large as the diameter of the neck of the flask, *B*. To determine the ratio of the two specific heats, the flask is filled with the gas under a pressure slightly greater than barometric pressure. The manometer *C* serves to measure the pressure of the gas within *A*. After the value of the pressure has been read on the manometer, the stop-cock *D* is opened momentarily to the air, thus permitting the pressure of the gas to fall adiabatically to that of the atmosphere. The stop-cock is then closed and the flask is allowed to stand for a few moments until its contents, which has cooled by adiabatic expansion, has regained the temperature of the room. The pressure on the manometer is then observed. Let the initial pressure of the gas be denoted by p_0, and atmospheric pressure by P. If the initial and final specific volumes are denoted by v_0 and v_1, then for an adiabatic process, we have

---

* Jour. de phys., **89**, 321, 428 (1819).

† Pogg. Ann., **127**, 497 (1866); **135**, 337, 527 (1868).

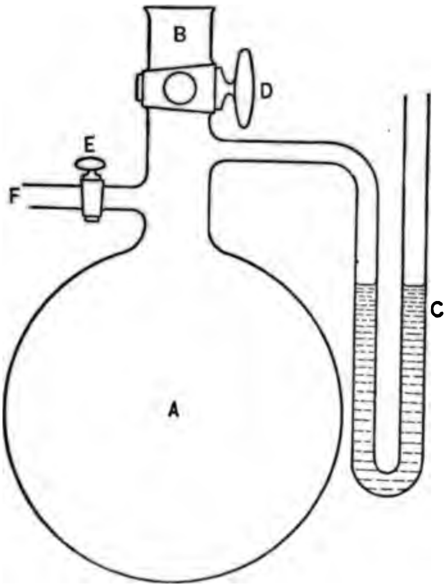


Fig. 21.

$$\frac{P}{p_0} = \left(\frac{v_0}{v_1}\right)^{\gamma}.$$

The value of the final specific volume is determined from the final pressure, p_1, by an application of Boyle's law, the pressure p_1 being developed isothermally.

Thus,

$$\frac{v_0}{v_1}=\frac{p_1}{p_0},$$

and consequently

$$\frac{P}{p_0}=\left(\frac{p_1}{p_0}\right)^\gamma,$$

or

$$\gamma=\frac{\log P-\log p_0}{\log p_1-\log p_0}.$$

Method of Kundt. According to the formula of Laplace for the velocity of transmission of a sound wave in a gas, we have

$$v=\sqrt{\gamma\frac{p}{d}},$$

in which p and d denote the pressure and density of the gas, and γ is the ratio of the two specific heats. If the wave velocities in two different gases, whose densities are d_1 and d_2 under the same conditions of temperature and pressure, be denoted by v_1 and v_2, we may write

$$\frac{v_1}{v_2}=\sqrt{\frac{\gamma_1 d_2}{\gamma_2 d_1}},$$

or replacing the densities of these gases by their respective molecular weights, M_1 and M_2, we have

$$\frac{v_1}{v_2}=\sqrt{\frac{\gamma_1 M_2}{\gamma_2 M_1}}. \qquad (1)$$

The ratio of the velocities of the two waves can be measured by means of the apparatus shown in Fig. 22. A wide glass tube about $1\frac{1}{2}$ meters in length is furnished with two side tubes, E and F. Into one end of the tube is inserted the glass rod BD which is clamped at its middle point by a tightly fitting cork, C. The other end of the tube is closed by means of the plunger A. A small amount of lycopodium powder is placed upon the bottom of the tube and is distributed uniformly by gently tapping the walls of the tube. The gas in which the velocity of the sound wave is to be determined is introduced into the tube through E, and the displaced air escapes at F. When the tube is filled, E and F are closed by means of rubber caps, and a piece of moistened chamois leather is drawn along BD causing it to vibrate longitudinally and to emit a shrill note. The vibrations are taken up by the gas in the tube and the powder arranges itself in a series of heaps corresponding to the nodes of vibration. If the nodes are not sharply defined, then A should be moved in or out until they become so. If λ_1 is the distance between two heaps or nodes, then $2\,\lambda_1$ will be the wave length of the note emitted by the rod BD, and if n represents the number of vibrations per second of the note emitted, we have for the velocity of sound in the gas

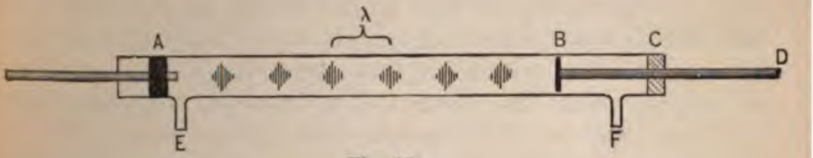


Fig. 22.

$$v_1 = 2\,n\lambda_1.$$

Similarly if a second gas be introduced into the tube we shall have

$$v_2 = 2\,n\lambda_2.$$

Therefore,

$$\frac{v_1}{v_2} = \frac{\lambda_1}{\lambda_2}. \qquad (2)$$

Substituting in equation (1), we have

$$\frac{\lambda_1}{\lambda_2} = \sqrt{\frac{\gamma_1 M_2}{\gamma_2 M_1}},$$

or

$$\gamma_1 = \gamma_2 \frac{\lambda_1^2}{\lambda_2^2} \cdot \frac{M_1}{M_2}. \qquad (3)$$

If the second gas is air, as is usually the case, $\gamma_2 = 1.405$ and $M_2 = 28.74$, (mol. wt. of hydrogen ÷ density of hydrogen referred to air, or $2 \div 0.0696 = 28.74$) or equation (3) becomes

883031

$$\gamma_1 = 1.405 \frac{\lambda_1^2}{\lambda_2^2} \cdot \frac{M_1}{28.74}.$$

Thus, γ for any gas can be determined by this method provided we know its value for another gas of known molecular weight.

Specific Heat of Gases and the Kinetic Theory. In terms of the kinetic theory, the energy of a gas may be considered to be made up of three parts: (1) the translational energy of the molecules, commonly termed their kinetic energy, (2) the intramolecular kinetic energy, and (3) the potential energy due to interatomic attraction within the molecules. When a gas is heated at constant volume all three of these factors of the total energy of the molecule may be affected. It is fair to assume, however, that when a monatomic gas, such as mercury vapor, is heated, all of the heat energy supplied is used to augment the translational kinetic energy of the molecules. As we have seen, the fundamental kinetic equation

$$pv = 1/3\, nmc^2$$

may be written

$$pv = 2/3 \cdot 1/2\, nmc^2,$$

and since $1/2\, nmc^2$ represents the total kinetic energy of the gas, we have

$$pv = 2/3 \text{ kinetic energy of 1 mol.},$$

or

$$\text{kinetic energy of 1 mol.} = 3/2\, pv.$$

But $pv = 2\,T$ calories, therefore

$$\text{kinetic energy of 1 mol.} = 3\,T \text{ cal.}$$

The kinetic energy of a constant volume of any gas at the temperatures T_1 and T_2, is given by the following equations: —

$$3/2\, p_1 v = 3\, T_1, \qquad (1)$$

and

$$3/2\, p_2 v = 3\, T_2. \qquad (2)$$

Subtracting (1) from (2) we obtain

$$3/2\, (p_2 - p_1)\, v = 3\, (T_2 - T_1), \qquad (3)$$

and for an increase in temperature of 1°, (3) becomes

$$3/2\, (p_2 - p_1)\, v = 3 \text{ cal.}$$

The molecular kinetic energy of one mole of a monatomic gas at constant volume is thus increased by 3 calories for each degree rise in temperature. As has already been shown,

$$M\ (c_p - c_v) = 2 \text{ cal.},$$

therefore, since $Mc_v = 3$ calories, $Mc_p = 3 + 2 = 5$ calories, and

$$\gamma = \frac{Mc_p}{Mc_v} = \frac{5}{3} = 1.66\,.$$

This value of γ is in perfect agreement with the results of the experiments on mercury vapor which is known to be monatomic. The converse of this method has been employed by Ramsay to prove that the rare gases of the atmosphere are monatomic, the value of γ for all of these gases being 1.66. In the case of polyatomic molecules the heat energy supplied is not only used in increasing their translational kinetic energy, but also in the performance of work within the molecule. The value of the internal work is indeterminate, but it is without doubt constant for any one gas. If the internal work be represented by a, then the value of the ratio of the two specific heats will be

$$\gamma = \frac{Mc_p}{Mc_v} = \frac{5 + a}{3 + a} < 1.66 > 1\,.$$

Reference to the table on p. 96, giving the value of γ for different gases, will show that this deduction from the kinetic theory is in perfect agreement with the experimental facts. With increasing complexity of the molecule, it is apparent that the amount of heat expended in doing internal work should increase, and therefore the specific heat should increase also. Inspection of the table confirms this deduction. The specific heat of monatomic gases is independent of the temperature while the specific heat of polyatomic gases increases slightly. These results may justly be regarded as among the greatest triumphs of the kinetic theory of gases.

PROBLEMS.

1. The volume of a quantity of gas is measured when the barometer stands at 72 cm., and is found to be 646 cc.: what would its volume be at normal pressure? *Ans.* 612 cc.

2. At what pressure would the gas in the preceding problem have a volume of 580 cc.? *Ans.* 80.19 cm.

3. A certain quantity of oxygen occupies a volume of 300 cc. at 0°: find its volume at 91°. *Ans.* 400 cc.

4. The weight of a liter of air under standard conditions is 1.293 grams: to what temperature must the air be heated so that it may weigh exactly 1 gram per liter? *Ans.* 79°.99.

5. At what temperature will the volume of a given mass of gas be exactly double what it is at 17°? *Ans.* 307°.

6. On heating a certain quantity of mercuric oxide it is found to give off 380 cc. of oxygen, the temperature being 23° and the barometric height 74 cm.; what would be the volume of the gas under standard conditions? *Ans.* 341.25 cc.

7. A liter of air weighs 1.293 grams under standard conditions. At what temperature will a liter of air weigh 1 gram, the pressure being 72 cm.? *Ans.* 61°.43.

8. A quantity of air at atmospheric pressure and at a temperature of 7° is compressed until its volume is reduced to one-seventh, the temperature rising 20° during the process: find the pressure at the end of the operation. *Ans.* 7.3 atmos.

9. The weight of a liter of nitrogen under standard conditions is 1.2579 grams. Calculate the specific gas constant, r. *Ans.* 3007 gr. cm.

10. The time of outflow of a gas is 21.4 minutes, the corresponding time for hydrogen is 5.6 minutes. Find the molecular weight of the gas. *Ans.* 29.2.

11. Calculate the molecular weight of chloroform from the following data: —

Weight of chloroform taken	0.220 gr.
Volume of air collected over water	45.0 cc.
Temperature of air	20°
Barometric pressure	755.0 mm.
Pressure of aqueous vapor at 20°	17.4 mm.

Ans. 121~~.1.~~

12. The density of a gas is 0.23 referred to mercury vapor. What is its molecular weight? *Ans.* 46.

13. Phosphorus pentachloride dissociates according to the equation

$$PCl_5 \rightleftarrows PCl_3 + Cl_2.$$

The molecular weight of PCl_5 is 208.28. At 182° the density is 73.5 and at 230° it is 62. Find the degree of dissociation at the two temperatures. *Ans.* $\alpha_{182°} = 0.417$, $\alpha_{230°} = 0.68$.

14. The specific heat at constant volume for argon is 0.075, and its molecular weight is 40. How many atoms are there in the molecule? *Ans.* 1.

15. What is the specific heat of carbon dioxide at constant volume, its molecular weight being 44 and the temperature 50°. *Ans.* 0.164.

16. The specific heat for constant pressure of benzene is 0.295: what is the specific heat for constant volume? *Ans.* 0.27.

CHAPTER VII.

LIQUIDS.

General Characteristics of Liquids. The most marked characteristic of the liquid state is that a given mass of liquid has a definite volume but no definite form. The volume of a liquid is dependent upon temperature and pressure but to a much smaller degree than is the volume of a gas. The formulas in which the volume of a liquid is expressed as a function of temperature and pressure are largely empirical, and contain constants dependent upon the nature of the liquid. This is undoubtedly due to the fact that in the liquid state the molecules are much less mobile than in the gaseous state. The distance between contiguous molecules being much less in liquids than in gases, the mutual attraction is increased while the mobility is correspondingly diminished. That liquids represent a more condensed form of matter than gases is shown by the change in volume which results when a liquid is vaporized: thus, 1 cc. of water at the boiling point when vaporized at the same temperature occupies a volume of about 1700 cc. A liquid contains less energy than a gas, since energy is always required to transform it into the gaseous state. Since gases can be liquefied by increasing the pressure and lowering the temperature, and since liquids can be vaporized by lowering the pressure and increasing the temperature, it is apparent that there is no generic difference between the two states of matter.

Connection Between the Gaseous and Liquid States. If a gas is compressed isothermally, its state may change in either of two ways depending upon the temperature: — (1) The volume at first diminishes more rapidly than the pressure increases, then in the same ratio and lastly more slowly. When the pressure attains a very high value the volume is but slightly altered. This case has already been considered in the preceding chapter. (2) The volume changes more rapidly than the pressure until, when a certain pressure is reached, the gas ceases to be homogeneous, partial liquefaction resulting. For a constant temperature, the pressure at which liquefaction occurs is invariable for a given gas, while the volume steadily diminishes until liquefaction is complete. Only when the whole mass of gas has been liquefied is it possible to increase the pressure and then, owing to the small compressibility of liquids, a large increase in pressure is required to produce a slight diminution in volume. If the temperature is above a certain point, dependent upon the nature of the gas, the phenomena of compression will follow (1); if below this point, the process will follow (2). That a gas may behave in either of the above ways was first clearly recognized by Andrews * in 1869, in connection with his experiments on the liquefaction of carbon dioxide. He found that if carbon dioxide was compressed, keeping the temperature at 0°, the volume changes more rapidly than the pressure, liquefaction resulting when a pressure of 35.4 atmospheres was reached. As the temperature was raised, he found that a higher pressure was required to liquefy the gas, until at temperatures above 30°.92 it was no longer possible to condense the gas to the liquid state. The temperature above which it was no longer possible to liquefy the gas he termed the *critical temperature*. In like manner the pressure required to liquefy the gas at the critical temperature, he termed the *critical pressure*, and the volume occupied by the gas or the liquid under these conditions he called the *critical volume*.

Isothermals of Carbon Dioxide. The results of Andrew's experiments † on the liquefaction of carbon dioxide are shown in Fig. 23, in which the ordinates represent pressures and the abscissæ the corresponding volumes at constant temperature. The curves obtained by plotting volumes against pressures at constant temperatures are called *isothermals*. For a gas which follows Boyle's law, the isothermals will be a series of equilateral hyperbolas. This condition is approximately fulfilled by air, for which three isothermals are given in the diagram. At 48°.1 the isothermal for carbon dioxide is nearly hyperbolic, but as the temperature becomes lower, the isothermals deviate more ar from those for an ideal gas. At the critical temperature,

---

* Trans. Roy. Soc. 159, 583 (1869).

† loc. cit.

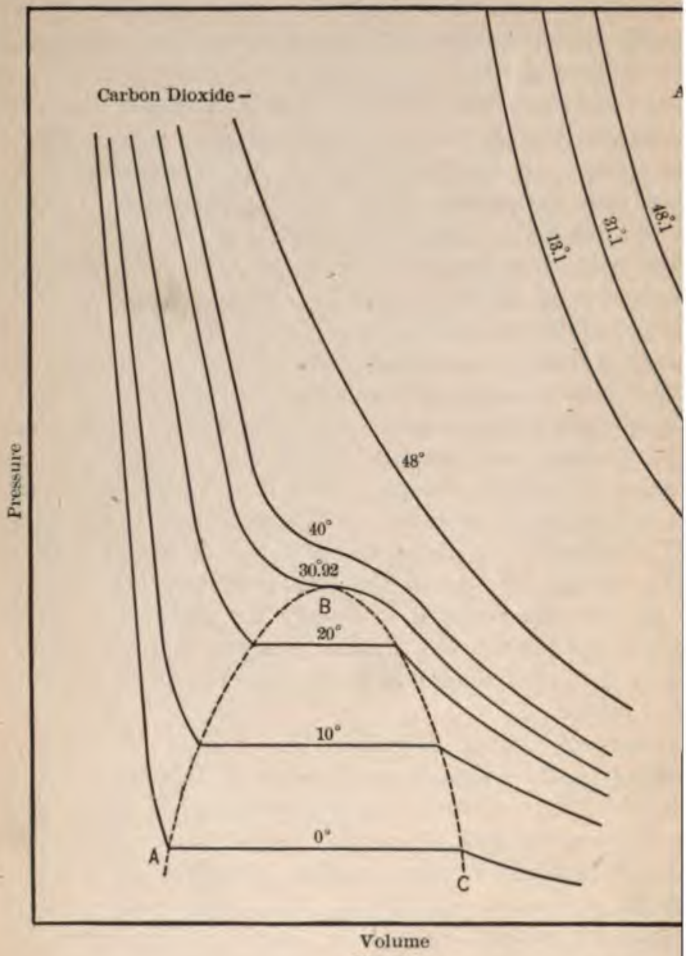


Fig. 23.

the curve is almost horizontal for a short distance, showing a very slight change in pressure there is an enormous s in volume. At still lower temperatures, 21°.1 and 13 orizontal portions of the curves are much more pronounced, ndicating that during liquefaction there is no change in pressure. When liquefaction is complete the curves rise abruptly, showing hat the change in volume is extremely small for a large increase n pressure; in other words the liquefied gas possesses a small coefficient of compressibility. At any point within the parabolic area, indicated by the dotted line ABC, both vapor and liquid are coexistent; at any point outside, only one form of matter, either liquid or vapor, is present. Andrew's experiments show that there is no fundamental difference between a gas and a liquid. It is apparent from the diagram that when carbon dioxide is subjected to great pressures above its critical temperature it behaves more like a liquid than a gas, in fact it is difficult to determine whether a highly compressed gas above its critical temperature should be classified as a gas or as a liquid.

Van der Waals' Equation and the Continuity of the Gaseous and Liquid States. In the preceding chapter we have learned that the fundamental gas equation

$$pv = RT$$

is only strictly applicable to an ideal gas, and that the] behavior of actual gases is represented with considerable accuracy, even at high pressures, by the equation of van der Waals,

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT$$

If this equation be arranged in descending powers of v, we have

$$v^3 - v^2\left(b + \frac{RT}{p}\right) + v\frac{a}{p} - \frac{ab}{p} = 0. \qquad (1)$$

This being a cubic equation has three possible solutions, each value of p affording three corresponding values of v; a, b, R and T being treated as constants. The three roots of this equation are either all real, or one is real and two are imaginary, depending upon the values of the constants. That is to say, at one temperature and pressure the values of a and b may be such, that v has three real values, while at another temperature and pressure, v may have one real and two imaginary values. In the accompanying

diagram, Fig. 22, a series of graphs of the equation for diffe
values of T is given. It will be observed that these curves l
a striking resemblance to the isotherms of carbon dioxide es
lished by the experiments of Andrews. In the case of the t
retical curves there are no sudden breaks such as appear in
actual discontinuous passage from the gaseous to the liquid st
Instead of passing from B to D along the wavelike path BaC
experiment has shown that the substance passes directly from
state B to the state D along the straight line BD. It is

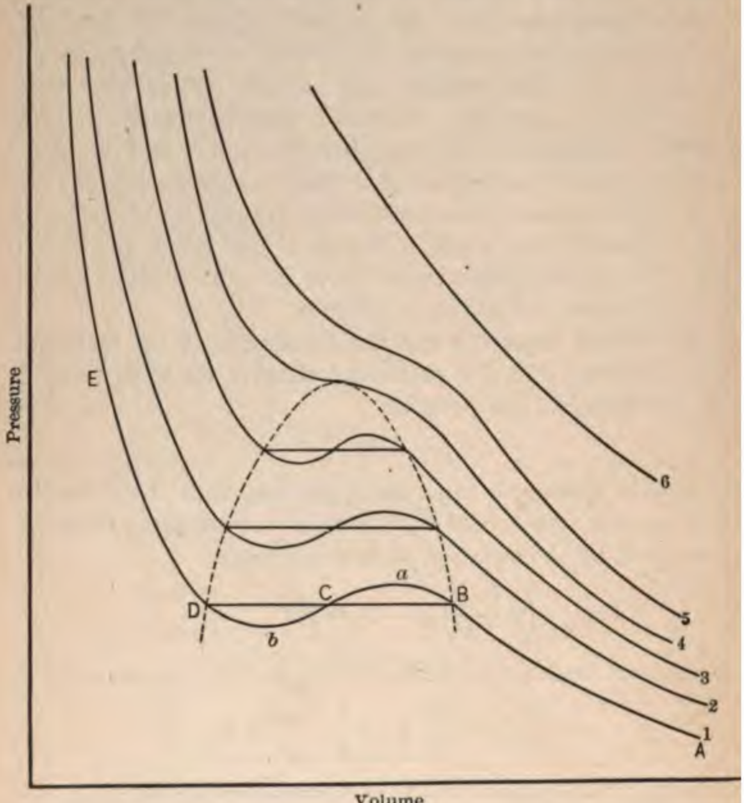


Fig. 24.

that van der Waals' equation fails to apply. As has been pointed out the substance between these two points is not homogeneous, being partly gaseous and partly liquid. Attempts have been made to realize the portion of the curve BaCbD experimentally. By studying supersaturated vapors and superheated liquids it has been found possible to follow the theoretical curve for short distances between B and D without discontinuity, but owing to the instability of the substance in this region, it is evident that the complete isothermal and continuous transformation of a gas into a liquid can never be effected. Van der Waals has called attention to the fact that in the surface layer of a liquid, where unique conditions prevail, it is quite possible that such unstable states may exist, and that there the transition from liquid to gas may in reality be a continuous process. The diagram shows that as T increases, the wave-like portion of the isothermals becomes less pronounced and eventually disappears, when the points B, C and D coalesce. At this point the three roots of the equation become equal, the volume of the liquid becoming identical with the volume of the gas. The substance at this point is in the critical condition. Since under these conditions the three roots of the equation

$$v^3 - \left(b + \frac{RT}{p}\right)v^2 + \frac{a}{p}v - \frac{ab}{p} = 0 \tag{1}$$

are equal, we may write $v_1 = v_2 = v_3 = v_c$, the subscript c indicating the critical state. Then equation (1) must be equivalent to

$$(v - v_c)^3 = v^3 - 3\,v_c v^2 + 3\,v_c^2 v - v_c^3 = 0. \tag{2}$$

Equating the corresponding coefficients of equations (1) and (2), we have

$$3\,v_c = b + \frac{RT_c}{p_c}, \tag{3}$$

$$3\,v_c^2 = \frac{a}{p_c} \tag{4}$$

and

$$v_c^3 = \frac{ab}{p_c}. \tag{5}$$

Dividing equation (5) by equation (4), we have

$$v_c = 3\,b, \tag{6}$$

and substituting this value in equation (4), we obtain

$$p_c = \frac{a}{27\,b^2}. \tag{7}$$

Lastly, substituting the values of v_c and p_c, given in equations (6) and (7), in equation (3), we have

$$T_c = \frac{8\,a}{27\,bR}. \tag{8}$$

Therefore,

$$\frac{p_c v_c}{T_c} = \frac{3}{8}R. \tag{9}$$

Or expressing the constants a, b and R in terms of the critical values of pressure, temperature and volume, we have

$$a = 3\,p_c v_c^2, \tag{10}$$

$$b = \frac{v_c}{3} \tag{11}$$

and

$$R = \frac{8\,p_c v_c}{3\,T_c}. \tag{12}$$

By means of equations (6), (7) and (8) it is possible to calculate the critical constants of a gas when the constants a and b of van der Waals' equation are known. If we take carbon dioxide as an example, for which $a = 0.00874$ and $b = 0.0023$ we obtain $v_c = 0.0069$ (observed value = 0.0066), $p_c = 61$ atmospheres, (observed value = 70 atmospheres), $T_c = 305°.5$ abs., (observed value 303°.9 abs.). Conversely by means of equations (10) and (11) the value of a and b can be calculated when the critical data are given.

Corresponding Conditions. If in the equation of van der Waals, the values of p, v and T be expressed as fractions of the corresponding critical values, we may write

$$p = \alpha p_c,$$
$$v = \beta v_c$$

and

$$T = \gamma T_c.$$

stituting these values in the equation

$$\left(p+\frac{a}{v^2}\right)\left(v-b\right)=RT,$$

ave

$$\left(\alpha p_c+\frac{a}{(\beta v_c)^2}\right)(\beta v_c-b)=R\gamma T_c,$$

l replacing p_c, v_c, and T_c by their values given in equations (6), and (8) of the preceding paragraph, we obtain

$$\left(\alpha+\frac{3}{\beta^2}\right)(3\,\beta-1)=8\,\gamma,$$

ich is van der Waals' *reduced equation of condition.*

In this equation everything connected with the individual ture of the substance has vanished, thus making it applicable all substances in the liquid or gaseous state in the same way at the fundamental gas equation is applicable to all gases irreective of their specific nature. It has been shown, however, at the equation is not entirely trustworthy and at best can be nsidered as little more than a rough approximation. The ief point to be observed in connection with this equation is at whereas for gases, the corresponding values of temperature, essure and volume, measured in the ordinary units, may be mpared, it is necessary in the case of liquids to make the comrison under *corresponding conditions.* For example, the molecar volumes of two liquids are to be compared, not at room mperature but at temperatures which are equal fractions of eir respective critical temperatures. Such temperatures van r Waals called *corresponding temperatures.*

By way of illustration, suppose we wish to compare alcohol d ether with respect to some particular property, such as rface tension. If the surface tension of alcohol be measured 60°, at what temperature must a similar measurement be ade with ether in order that the results may be comparable? he critical temperature of alcohol is 243° C. or 516° absolute; at of ether is 194° C. or 467° absolute. Then according to van er Waals' definition of corresponding conditions, the temperature,

t, at which measurements should be made with ether will be gi by the proportion, $273 + t : 467 :: 273 + 60 : 516$, or $t = 28$° By making comparisons of various properties at correspond temperatures it has been found that greater regularities observed than when comparisons are made at the same tempe ture, thus justifying the claim of van der Waals.

Liquefaction of Gases. The history of the liquefaction gases has for a long time been regarded as one of the m interesting chapters of physical science. Among the first succe ful workers in this field was Faraday.* He liquefied practica all of the gases which condense under moderate pressures and not very low temperatures. A sketch of the apparatus used Faraday is shown in Fig. 25. It consisted of an invert V-shaped tube, in one end of which was placed some solid wh would liberate the desired gas on heating, while the other e was sealed and immersed in a freezing mixture. When the su stance at *A* had been heated long enough to liberate considera gas, the pressure within the tube became sufficiently high to ca the gas to liquefy at the temperature of the end *B*. Thus chlor

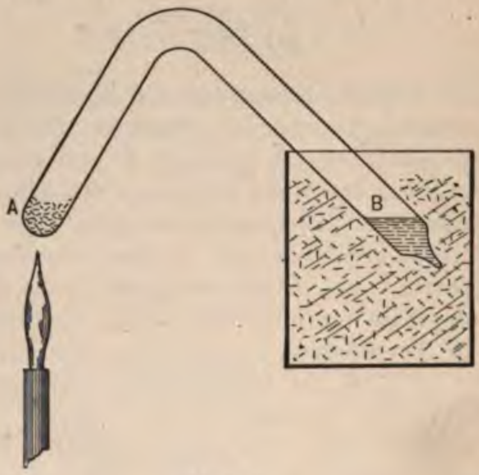


Fig. 25.

---

* Phil. Trans. 113, 189 (1823).

te was heated in the tube and the liberated chlorine was
nsed at B as a yellow liquid. In 1834, Thilorier[*] succeeded
uefying carbon dioxide in quite large amounts by the use of
form of apparatus. In connection with his experiments
uid carbon dioxide, he observed that when it was allowed to
ize, enough heat was absorbed to lower the temperature
its freezing point, solid carbon dioxide being obtained. He
vered that a mixture of solid carbon dioxide and ether was a
rful refrigerant, and that under diminished pressure the
ure gave temperatures ranging from − 100° C. to − 110° C.
mixture is known today as *Thilorier's mixture.* Faraday[†]
rtook the liquefaction of the so-called permanent gases in 1845.
this second series of experiments by Faraday he employed
r pressures than in his earlier experiments, and also made
f the newly discovered Thilorier mixture as a refrigerant.
as partially successful in his attempt to liquefy the hitherto
ondensible gases. He liquefied ethylene, phosphine and
obromic acid and also solidified ammonia, cyanogen, and
us oxide. He failed to liquefy hydrogen, oxygen, nitrogen,
oxide and carbon monoxide. No further advance in the
faction of gases was made until the year 1869 when Andrews
ed out the importance of cooling the gas below its critical
erature. This discovery explained why so many of the
r experiments had failed, and opened the way to the brilliant
sses of the latter part of the nineteenth century. In 1877,
etet[‡] and Pictet,[§] working independently, succeeded in
fying oxygen. Cailletet subjected the gas to a pressure of
t 300 atmospheres using boiling sulphur dioxide as a refriger-
The gas was further cooled by suddenly releasing the pres-
and allowing it to expand. In addition to oxygen he also
fied air, nitrogen and possibly hydrogen. Shortly afterward
83, the Polish scientists, Wroblewski and Olszewski,[¶] pub-

---

[*] Lieb. Ann., **30**, 122 (1839).

[†] Phil. Trans., **135**, 155 (1845).

[‡] Compt. rend., **85**, 1217 (1877).

[§] Ibid., **85**, 1214, 1220 (1877).

[¶] Wied. Ann., **20**, 243 (1883).

lished an account of their interesting and highly importan In their experiments they subjected the gas to be liquefied pressure, and simultaneously cooled it to a very low tempe Among the refrigerants used by them was liquid ethylene was allowed to boil off under diminished pressure, giving a t ature of – 130° C. At this temperature, a pressure o 20 atmospheres was sufficient to condense oxygen to the state. Having liquefied oxygen, nitrogen, air and carbo oxide, and having determined the boiling-points of thes under atmospheric pressure, they proceeded to use these li gases as refrigerants, allowing them to boil off under dim pressure, thus obtaining temperatures as low as – 200° very small amount of liquid hydrogen was obtained in thi Subsequent attempts by these same experimenters to hydrogen, while not much more successful than their attempts, enabled them to determine its boiling-point. after the publication of the first papers of Wroblews Olszewski, Dewar * devised a new form of apparatus for fying air, oxygen and nitrogen on a comparatively large He also introduced the well-known vacuum-jacketed flas tubes which greatly facilitated carrying out experiment liquefied gases. In 1895, Linde in Germany and Ham England simultaneously and independently constructed m for the liquefaction of air in large quantities.

In the method devised by these experimenters the air subjected to a preliminary cooling, produced by the rapid e tion of a liquefied gas under diminished pressure, as in the m of Wroblewski and Olszewski. In the Linde liquefier, th compressed to about 200 atmospheres. It is then passed t a chamber containing anhydrous calcium chloride to rem greater part of the moisture, after which it is cooled by allo to circulate through a coiled pipe immersed in a freezing m Nearly all of the moisture remaining in the air is deposited walls of the pipe in the form of frost. The air then enters spiral tube jacketed with a non-conducting material, and i allowed to expand to a pressure of about 15 atmos

---

* Proc. Roy. Inst., 1886, 550.

During this expansion the temperature of the air is appreciably lowered. When the air has traversed the spiral tube, it is still further cooled by allowing it to expand to a pressure equal to that of the atmosphere. The air which has been thus cooled is then passed backward through the annular space between the spiral tube and a concentric jacket, thus cooling the entering portion of air. Consequently this next portion of air expands from a lower initial temperature, and the cooling effect is increased. In like manner, when this cooler air passes backward it cools still further the next succeeding portion, and eventually the temperature is reduced sufficiently to cause a small amount of the air to liquefy as it issues from the end of the spiral tube. The remaining portion of the air which has not been liquefied, passes backward through the annular tube and cools the following portion to a still greater extent, causing a larger proportion to liquefy on expansion. With a 3-horse-power machine, a continuous supply of 0.9 liter per hour can be obtained. Further improvements in this apparatus have been made by Dewar and Hampson, and by means of it Dewar's brilliant successes in the liquefaction of gases have been achieved.

The most efficient apparatus for the liquefaction of air and other gases is that developed by Claude.* The essential features of his liquefier are shown in Fig. 26. The air is first compressed to 40 atmospheres pressure by means of an ordinary compression pump not shown in the diagram, the moisture and carbon dioxide being removed as in Linde's method. It then enters the tube *A*, which in reality is of a spiral form, and divides at *B*. A portion enters the cylinder *D* through a valve chest similar to that in a steam engine forces out the piston and causes the wheel, *W*, to revolve, thereby doing work and cooling the air. The cooled air escapes from the valve chest and circulates through the liquefying chamber *L*, where it causes the portion of compressed air entering at *B* to liquefy. It then issues from the liquefier and traverses *M*, cooling the entering portion of air in *A*, and finally returns to the compressor. The pressure of the air when it issues from *D* is almost atmospheric, and its temperature is below − 140° C. About twenty-five per cent of the power consumed in compression is regained by the motor. The apparatus produces about 1 liter of liquid air per horse-power hour. By means of this improved apparatus, based upon the regenerative principle, all known gases have now been liquefied, the last to succumb being helium which was liquefied in 1908, by Kammerlingh Onnes in the Leyden cryogenic laboratory. The subjoined table gives the critical data together with the boiling and freezing temperatures of some of the more common gases.

---

* Compt. rend., II, 500 (1900); I, 1568 (1902); II, 762, 823, (1905).

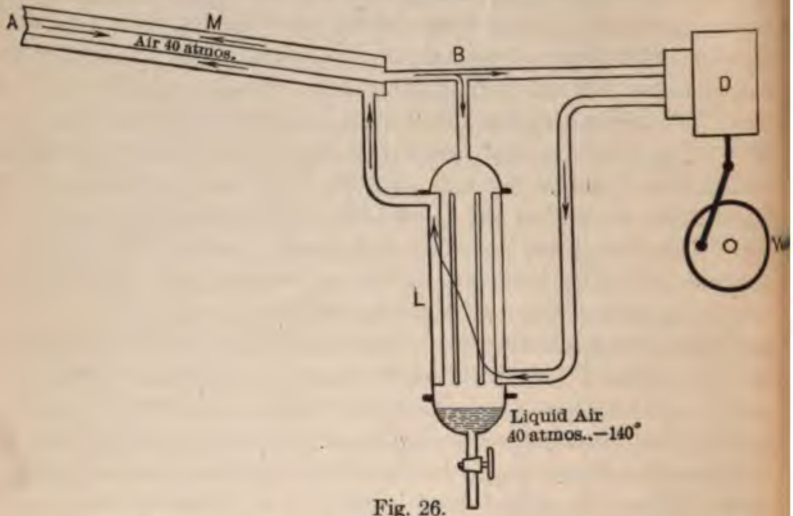


Fig. 26.

CRITICAL DATA FOR GASES.

Gas.	Crit. Temp.	Crit. Press. (Atmos.)	Boiling Point (at 760 mm.).	Freezing Point.
Helium	−267°	....	....	....
Hydrogen	−242°	20	−252°.5	−258°.9
Air	−140°	39	−191°	....
Nitrogen	−146°	35	−195°.5	−210°.5
Oxygen	−118°	50.8	−182°.8	−227°
Carbon monoxide	−141°	36	−190°	−207°
Nitric oxide	− 96°	64	−153°.6	−167°
Carbon dioxide	+ 31°	73	− 78°	− 65°
Hydrochloric acid	+ 51°.3	81.5	− 35°	−116°
Ammonia	+130°	115	− 33°.7	− 77°

Vapor Pressure of Liquids. According to the kinetic theory there is a continuous flight of particles of vapor from the surface of a liquid into the free space above it. At the same time the reverse process of condensation of vapor particles at the surface of the liquid is taking place. Eventually a condition of equilibrium will be established between the liquid and its vapor, when the rate of escape will be exactly counterbalanced by the rate of condensation of vapor particles. The pressure exerted by the vapor of a liquid when equilibrium has been attained is known as its *vapor pressure*. The equilibrium between a liquid and its vapor is dependent upon the temperature. For every temperature below the critical temperature, there is a certain pressure at which vapor and liquid may exist in equilibrium in all proportions; and conversely for every pressure below the critical pressure, there is a certain temperature at which vapor and liquid may exist in equilibrium in all proportions. This latter temperature is termed the boiling-point of the liquid. The vapor pressure of a liquid may be measured directly by placing a portion of it above the mercury in the vacuum of a barometer tube, heating to the desired temperature, and observing the depression of the mercury column. This is known as the *static method*. It is open to the objection that the presence of volatile impurities in the liquid causes too great depression of the mercury column, the vapor pressure of the impurity adding itself to that of the liquid whose vapor pressure is sought. A better method for the measurement of vapor pressure is that known as the *dynamic method*. In this method the pressure is maintained constant and the boiling temperature is determined with an accurate thermometer. The boiling temperatures corresponding to various pressures may be measured, provided we have a suitable device for changing and measuring the pressure. The results obtained by the static and dynamic methods agree closely if the liquid is pure, but if volatile impurities are present the results obtained by the dynamic method are more trustworthy. A method for the measurement of vapor pressure due to James Walker * is of considerable interest. In this method, a current of pure dry air is bubbled through a weighed amount of the liquid whose vapor pressure is to be determined. The liquid is maintained at constant temperature and its loss in weight is observed. In passing through the liquid the air will absorb an amount of vapor directly proportional to the vapor pressure of the liquid. If 1 mol of liquid is absorbed by v liters of air, then we have

---

* Zeit. phys. Chem., 2, 602 (1888).

$$pv = RT,$$

where p is the vapor pressure of the liquid, and T its temperature. If v_1 is the volume of air which absorbs g grams of the vapor of the liquid whose molecular weight is M, then

$$pv_1 = \frac{g}{M} RT,$$

or

$$p = \frac{g}{Mv_1} RT.$$

In this equation, v_1 denotes the total volume containing g grams of the liquid in the form of vapor, or in other words it represents the air and vapor together. Since the volume of the air is in general so much greater than that of the vapor, v_1 may be taken as that of the air alone.

Heat of Vaporization. In order to transform a liquid into a vapor a large amount of heat is required. Thus, when a liquid is heated to the boiling-point, the volume must be increased against the pressure of the atmosphere, external work being done, and when the boiling temperature is reached the liquid must be vaporized; the heat expended in causing the change of physical state being much greater than that required to expand the liquid. An interesting relation between the heat of vaporization and the absolute boiling-point of a liquid was discovered by Trouton.* If T denotes the absolute boiling-point and w the heat of vaporization of 1 gram of liquid whose molecular weight is M, then according to Trouton

$$\frac{Mw}{T} = 21,$$

or in words, the ratio of the molecular heat of vaporization to the absolute boiling temperature of a liquid is constant, the numerical value of the ratio being approximately 21. This is known as Trouton's law. While this relation holds quite well for many liquids, Nernst has pointed out that the constant varies with the temperature, and has proposed two other forms of the equation. Bingham has simplified the equations of Nernst to the following form: —

---

* Phil. Mag. (5), 18, 54 (1884).

$$\frac{Mw}{T} = 17 + 0.011\,T.$$

While this modification of the Trouton equation has been found to hold for a large number of substances, there are other substances for which the left side of the equation has a value greater than that of the right side. Bingham infers that where this occurs, the substance in the liquid state has a greater molecular weight than it has in the gaseous state, or in other words, the liquid is associated. It is evident that an associated liquid will require an expenditure of energy over and above that required for vaporization, to break down the molecular complex. The difference between the values of the two sides of the equation may be taken as a rough measure of the degree of association.

Boiling-Point and Critical Temperature. An interesting relation has been pointed out by Guldberg * and Guye.† These two investigators have shown that the absolute boiling temperature of a liquid is about two-thirds of its critical temperature. That this empirical relation holds for a variety of different substances is shown in the accompanying table.

RELATION OF BOILING-POINT TO CRITICAL TEMPERATURE.

Substance.	T_b	T_c	T_b/T_c
Oxygen	90°	155°	0.58
Chlorine	240°	414°	0.58
Sulphur dioxide	263°	429°	0.61
Ethyl ether	308°	467°	0.66
Ethyl alcohol	351°	516°	0.68
Benzene	353°	562°	0.63
Water	373°	637°	0.59
Phenol	454°	691°	0.66

---

* Zeit. phys. chem., **5**, 376 (1890).

† Bull. Soc. Chim., (3), **4**, 262 (1890).

Molecular Volume. In dealing with the volume relations of liquids it is customary to employ the *molecular volume*, i.e., the volume occupied by the molecular weight of the liquid in grams. The justification of this procedure is that when we compare the gram-molecular weights of liquids, the comparison involves equal numbers of molecules of the different substances. Since

$$\text{volume} = \frac{\text{mass}}{\text{density}},$$

we may write

$$\text{molecular volume} = \frac{\text{molecular weight}}{\text{density}},$$

and similarly,

$$\text{atomic volume} = \frac{\text{atomic weight}}{\text{density}}.$$

Relations between the molecular volumes of liquids were first pointed out by Kopp.* On comparing the molecular volumes of different liquids at their boiling-points, he found that constant differences in composition correspond to constant differences in the molecular volumes. Thus the molecular volumes of the successive members of an homologous series differ by the same number of units, this difference corresponding, for example, to a CH_2 group. In like manner the molecular volumes of various groups have been determined, and from these in turn the atomic volumes of the constituent elements have been worked out. The atomic volumes assigned by Kopp to some of the elements commonly entering into organic compounds are as follows: —

$C = 11$ Cl = 22.8 I = 37.5 Hydroxyl O = 7.8
$H = 5.5$ Br = 27.8 S = 22.6 Carbonyl O = 12.2

The value of the atomic volume is found to be dependent upon the manner of linkage; thus oxygen in the hydroxyl group has the atomic volume, 7.8, while oxygen in the doubly linked condition, as in the carbonyl group, has the atomic volume, 12.2. By means of such a table of experimentally determined atomic

---

[*] Lieb. Ann., **41**, 79 (1842); **96**, 153, 303 (1855); **96**, 171 (1855).

volumes, Kopp showed that it is possible to calculate the molecular volume of a liquid with a fair degree of accuracy. For example, the molecular volume of acetic acid $C_2H_4O_2$, may be calculated from the atomic volumes of its constituent atoms as follows: —

$$\begin{aligned} 2\,\mathrm{C} = 2 \times 11 &= 22 \\ 4\,\mathrm{H} = 4 \times 5.5 &= 22 \\ 1\ \text{Hydroxyl O} = 1 \times 7.8 &= 7.8 \\ 1\ \text{Carbonyl O} = 1 \times 12.2 &= \underline{12.2} \\ \text{Molecular volume} &= 64.0 \end{aligned}$$

The density of acetic acid at its boiling-point is 0.942, and its molecular weight is 60, therefore the observed value of the molecular volume is $60 \div 0.942 = 63.7$, a result which is in excellent agreement with that calculated from the atomic volumes of the constituents. The more recent investigations of Thorpe, Lossen, Schiff and Buff afford a confirmation of the conclusion reached by Kopp, that the molecular volumes of liquids are in general additive. While Kopp found that his results were most regular when the molecular volumes were determined at the boiling temperatures of the respective liquids, the reason for this did not appear until after van der Waals had developed his theory of corresponding states. As has been pointed out in the preceding paragraph the boiling-points of most liquids are approximately two-thirds of their respective critical temperatures, and therefore the boiling-points are corresponding temperatures.

Co-volume. By studying various series of hydrocarbons, alcohols and ethers, Traube * has been led to suggest that the molecular volume of a liquid be looked upon as made up of the atomic volumes of its constituent elements and a magnitude which he terms the *co-volume*. This latter he defines as the space surrounding a molecule within which it is free to vibrate and from which other molecules are excluded. The co-volume appears to be nearly constant for a large number of substances, its mean value at a temperature of 15° C. being 25.9 cc. The values assigned by Traube to the atomic volumes of some of the elements are as follows: —

---

* Uber den Raum der Atome. J. Traube. Ahrens' Sammlung Chemischer und chemisch-technischer Vortraege, 4, 255 (1899).

C = 9.9 O = 5.5 Br = 17.7 N (trivalent) = 1.5
H = 3.1 Cl = 13.2 I = 21.4 N (pentavalent) = 10.7

Traube has worked out a series of constants which must be deducted to allow for ring formation and for double and treble linking. By means of these values, it is possible to calculate the molecular volume of a substance by adding together the respective atomic volumes of the constituents of the liquid and the co-volume, 25.9. It is of course necessary to know the molecular weight of the substance together with its constitution, so that due allowance may be made for unsaturation. For example, the molecular volume of ethyl ether, $C_4H_{10}O$, may be calculated by Traube's method as follows: —

$$\begin{array}{rr}
4\,\mathrm{C} = 4 \times 9.9 = & 39.6 \\
10\,\mathrm{H} = 10 \times 3.1 = & 31 \\
1\,\mathrm{O} = 1 \times 5.5 = & \underline{5.5} \\
 & 76.1 \\
\text{Co-volume} & \underline{25.9} \\
\text{Molecular volume} & 102.0
\end{array}$$

The molecular volume, as determined from the molecular weight and density at 15° C., is 74 ÷ 0.7201 = 102.7.

The method of Traube may be employed in roughly checking the accepted value of the molecular weight of a liquid provided its density at 15° C. is known, since in the equation

$$M/d = \Sigma \text{ atomic volumes} + 25.9, \text{ expressing Traube's relation,}$$

M is the only unknown quantity. It is apparent that the liquid must be non-associated, since for an associated substance the normal co-volume must necessarily accompany the polymerized molecule. In this case the formula becomes

$$M/d = \Sigma \text{ atomic volumes} + 25.9/n,$$

where n denotes the number of simple molecules in the polymer. Obviously when the molecular weight of a liquid is known, the experimental determination of the co-volume, ($M/d - \Sigma$ atomic vols.) may be used to estimate the degree of association. The values thus obtained are not in satisfactory agreement with the factors of association derived by means of other methods.

Refractive Power of Liquids. The velocity of transmission of light through any medium depends upon its nature, especially upon its density. When a ray of light passes from one medium into another it is refracted, the degree of refraction being such that the ratio of the sines of the angles of incidence and refraction is constant and characteristic for the two media. This

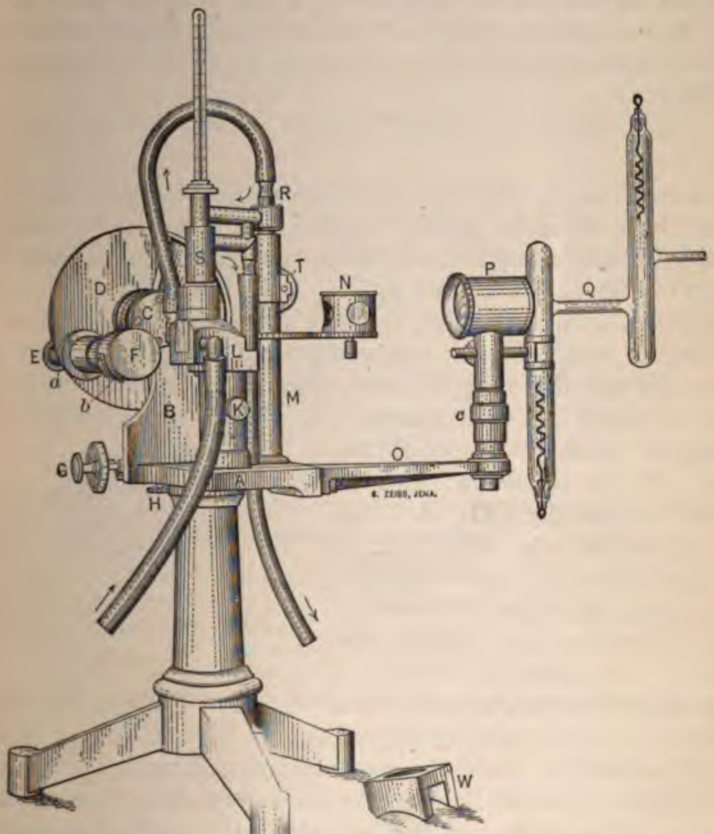


Fig. 27.

fundamental law of refraction was discovered by Snell about 1621. According to the wave theory of light, the ratio of the sines of the angles of incidence and refraction is identical with the ratio of the velocities of light in the two media. The ratio is termed the *index of refraction* and is usually denoted by the letter n. Representing by i and r, the angles of incidence and refraction, and by v_1 and v_2, the respective velocities of light in the two media, we have

$$n = \frac{\sin i}{\sin r} = \frac{v_1}{v_2}.$$

Various forms of apparatus have been devised for the determination of the refractive index of liquids. Of these the best known and most satisfactory is the refractometer of Pulfrich, an improved form of which is shown in Fig. 27. While the limits of this book prohibit a detailed description of the apparatus, the fundamental principles involved in its construction will be readily understood from the accompanying diagram, Fig. 28. The liquid or fused solid is placed in a small glass cell, C, which is cemented to a rectangular prism of dense optical glass, P, the refractive index of which is generally 1.61. A beam of monochromatic light, from a sodium flame or a spectrum-tube containing hydrogen, is allowed to enter the prism in a direction parallel to the horizontal surface of separation between the glass and the liquid. After passing through the liquid and the prism, the beam emerges making an angle i with its original direction. By means of a telescope, the emergent beam can be observed and its position noted, the angle of emergence being read on a divided circle attached to the telescope. From the angle of emergence thus determined, the index of refraction of the liquid can be calculated in the following manner. The value of the index of refraction, N, for air/glass being known, we have

$$N = \frac{\sin i}{\sin r}. \tag{1}$$

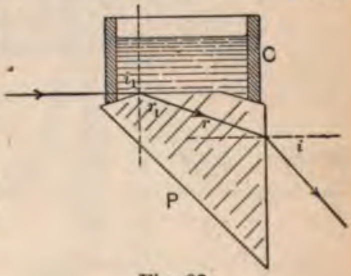


Fig. 28.

The angle of incidence of the last ray entering the prism from the liquid is 90°, or $\sin i_1 = 1$. The index of refraction, n_1, for liquid/glass may be calculated thus,

$$n_1 = \frac{\sin i_1}{\sin r_1} = \frac{1}{\sin r_1}. \tag{2}$$

But

$$\sin r_1 = \cos r = \sqrt{1 - \sin^2 r}. \tag{3}$$

Transposing equation (1) and substituting in equation (3), we have

$$\sin r_1 = \sqrt{1 - \frac{\sin^2 i}{N^2}},$$

or

$$\sin r_1 = \frac{1}{N}\sqrt{N^2 - \sin^2 i}. \tag{4}$$

Therefore, substituting equation (4) in equation (2), we have

$$n_1 = \frac{N}{\sqrt{N^2 - \sin^2 i}}. \tag{5}$$

Remembering that $n = N/n_1$, we have for the index of refraction, n, for air/liquid, by substitution in equation (5),

$$n = \sqrt{N^2 - \sin^2 i},$$

or if $N = 1.61$,

$$n = \sqrt{2.5921 - \sin^2 i}.$$

The values of $\sqrt{N^2 - \sin^2 i}$ are generally given, for different values of i, in tables supplied with the refractometer, thus saving the experimenter a somewhat laborious calculation. The value of n thus obtained is the index of refraction from air into the liquid; if the index from vacuum into the liquid, the so-called *absolute index*, is required, the value of n must be multiplied by 1.00029. The index of refraction is dependent upon temperature, pressure and in general upon all conditions which affect the density of the medium. Furthermore, it is dependent upon the wave-length of the light employed, the index for the red rays being greater than that for the violet rays. It is therefore necessary in making measurements of refractive indices to use light of a definite wave-length, or what is termed *monochromatic light*. The sodium flame is most frequently used for this purpose, the wave-length being represented by the letter *D*. Measurements of the refractive index referred to the *D*-line of sodium are commonly designated by the symbol n_D. When incandescent hydrogen is employed as a source of light, the refractive index may be determined for the *C*-, *F*- and *G*-lines, the respective values being represented by n_C, n_F, and n_G.

Specific and Molecular Refraction. Various attempts have been made to express the refractive power of a liquid by a formula which is independent of variations of temperature and pressure. Of the different formulas proposed but two need be mentioned. The first, due to Gladstone and Dale,* is as follows: —

$$r_1 = \frac{n-1}{d},$$

in which d denotes the density of the liquid and r_1 is the so-called *specific refraction*. The other formula, proposed by Lorenz † and Lorentz,‡ has the following form: —

$$r_2 = \frac{1}{d} \cdot \frac{n^2-1}{n^2+2}.$$

This formula is superior to that of Gladstone and Dale which is purely empirical. It is based upon the electromagnetic theory of light and gives values of r_2 which are quite independent of the temperature. In order that we may compare the refractive powers of different liquids, the specific refractions are multiplied by their respective molecular weights, the resulting products being termed their *molecular refractions*. As the result of a large number of experiments, it has been shown that the molecular refraction of a compound is made up of the sum of the refractive constants of the constituent atoms, or in other words refractive power is an additive property. The values of the refractive constants of the elements and commonly-occurring groups have been determined with great care by Brühl and others, the method employed being similar to that used by Kopp in connection with his investigations on molecular volumes. Thus, Brühl found in the homologous series of aliphatic compounds that a difference of CH_2 in composition corresponds to a constant difference of 4.57 in molecular refraction. Then, having determined the molecular refraction of a ketone or an aldehyde of the composition, $C_nH_{2n}O$, he subtracted n times the value of CH_2 and obtained the atomic refraction of carbonyl oxygen. By deducting the molecular refraction of the hydrocarbon, C_nH_{2n+2}, from that of the corresponding alcohol, $C_nH_{2n+2}O$, he obtained the atomic refraction of hydroxyl oxygen. By subtracting six times the value of CH_2 from the molecular refraction of hexane, C_6H_{14}, he obtained the refractive constant for hydrogen or 2 H = 2.08. In like manner the refractions of other elements and groups of elements were determined.

---

* Phil. Trans. (1858).

† Wied. Ann., **11**, 70 (1880).

‡ Ibid., **9**, 641 (1880).

Just as in the case of molecular volumes so with molecular refractions, the arrangement of the atoms in the molecule must be taken into consideration. Brühl,* who has devoted much time to the investigation of the effect of constitution upon refraction, has pointed out that the molecular refraction of compounds containing double and triple bonds is greater than the calculated value, and he has assigned to these bonds definite constants of refraction. The values of the atomic refractions for a few of the elements as given by Brühl are as follows: —

C = 2.48
H = 1.04
Cl = 6.02
I = 13.99
Hydroxyl O = 1.58
Carbonyl O = 2.34
Double bond = 1.78
Triple bond = 2.18

More recent investigations bring out the fact that, when double or triple bonds occupy adjacent positions in the molecule, the simple additive relations no longer obtain. The determination of the molecular refraction of a liquid affords a means of ascertaining or confirming its chemical constitution. For example, geraniol has the formula $C_{10}H_{18}O$, and its chemical behavior is such as to warrant the conclusion that it is a primary alcohol. The value of n_D is 1.4745, from which the molecular refraction is calculated to be 48.71. The molecular refraction calculated from the atomic refractions given in the preceding table is: —

---

* Proc. Roy. Inst., 18, 122 (1906).

$$\begin{array}{r} 10\,\mathrm{C} = 10 \times 2.48 = 24.80 \\ 18\,\mathrm{H} = 18 \times 1.04 = 18.72 \\ 1\ \text{Hydroxyl O} = 1 \times 1.58 = \underline{1.58} \\ \text{Molecular refraction } 45.10 \end{array}$$

The difference between the theoretical and experimental values of the molecular refraction is $48.71 - 45.10 = 3.61$, which is approximately twice the value of a double bond, $1.78 \times 2 = 3.56$. From this we conclude that the molecule of geraniol contains two double bonds. Furthermore an alcohol of the formula, $C_{10}H_{18}O$, containing two double bonds cannot possess a ring structure and therefore must be a member of the aliphatic group of compounds. This conclusion is supported by the chemical properties of the substance.* In a similar manner the Kekulé formula for benzene has been confirmed, the difference between the theoretical and experimental values of the molecular refraction indicating the presence of three double bonds in the molecule.

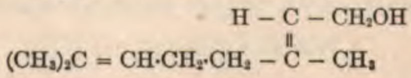
Specific Refraction of Mixtures. The specific refraction of an homogeneous mixture or solution is the mean of the specific refractions of its constituents. Thus, if the specific refractions of the mixture and its two components are represented by r_1, r_2, and r_3, then

$$r_1 = \frac{p}{100} r_2 + \frac{(100 - p)}{100} r_3,$$

where p denotes the percentage of the constituent whose specific refraction is r_2. Hence it is possible to determine the specific refraction of a substance in solution by measuring the refractive indices and densities of the solution and solvent. If the refractive indices of the solvent, solution and dissolved substance are

---

* The accepted structural formula of geraniol is



$$\begin{array}{l} \qquad\qquad\qquad\qquad\quad H-C-CH_2OH \\ \qquad\qquad\qquad\qquad\qquad\ \ \| \\ (CH_3)_2C=CH\cdot CH_2\cdot CH_2-C-CH_3 \end{array}$$

represented by n_1, n_2, and n_3 respectively, and if d_1, d_2, and d_3 denote the corresponding densities, then we have

$$\frac{1}{d_3}\cdot\frac{n_3^2-1}{n_3^2+2}=\frac{100}{d_2p}\cdot\frac{n_2^2-1}{n_2^2+2}-\frac{100-p}{d_1p}\cdot\frac{n_1^2-1}{n_1^2+2},$$

where p is the percentage of the dissolved substance. As has already been mentioned, the formula of Lorenz-Lorentz is based upon the electromagnetic theory of light. According to this theory $n^2 - 1/n^2 + 2$ expresses the fraction of the unit of volume of the substance which is actually occupied by it. From this it follows that the molecular refraction, $\frac{M}{d}\cdot\frac{n^2-1}{n^2+2}$, is an expression of the volume actually occupied by the atomic nuclei of the molecule. It is interesting to note that the ratio of the sum of the atomic volumes, calculated by the method of Traube, to the corrected molecular volume, as determined by the Lorenz-Lorentz formula, is approximately constant, or

$$\frac{\Sigma \text{ atomic volumes}}{\frac{M}{d}\cdot\frac{n^2-1}{n^2+2}}=3.45 \text{ approximately.}$$

This may be considered as the ratio of the volume within which the atoms execute their vibrations to their actual material volume.

Rotation of the Plane of Polarized Light. Some liquids when placed in the path of a beam of polarized light possess the property of rotating the plane of polarization to the right or to the left. Such liquids are said to be *optically active*. Those substances which rotate the plane of polarization to the right are termed *dextro-rotatory*, while those which cause an opposite rotation are called *levo-rotatory*. The determination of the rotatory power of a liquid is made by means of an instrument known as a *polarimeter*, a convenient form of which is shown in Fig. 29. The essential parts of this instrument are two similar Nicol prisms placed one behind the other with their axes in the same straight line. The light after passing through the forward prism, P, known as the *polarizer*, has its vibrations reduced to a single plane; it is said to be plane polarized. On entering the rear Nicol prism, A, known as the *analyzer*, the light will either pass through or be completely stopped, depending upon the position of the prism. If the analyzer be slowly rotated, it will be observed that the positions of maximum transmission and extinction occur at points 90° apart. If the analyzer be rotated, so that its axis is at right angles to the axis of the polarizer, the field observed will be dark, no light being transmitted. If now a tube similar to that shown in Fig. 30 be filled with an optically active liquid and placed between the polarizer and analyzer, the field will become light again, due to the rotation of the plane of polarization by the optically-active substance. The extent to which the plane of polarization has been rotated can be determined by turning the analyzer until the field becomes dark again, and reading on the divided circle, *K*, the number of degrees through which it has been moved. When it is necessary to turn the analyzer to the right, the substance is dextro-rotatory, and when it is necessary to turn it to the left, the substance is levo-rotatory. Various

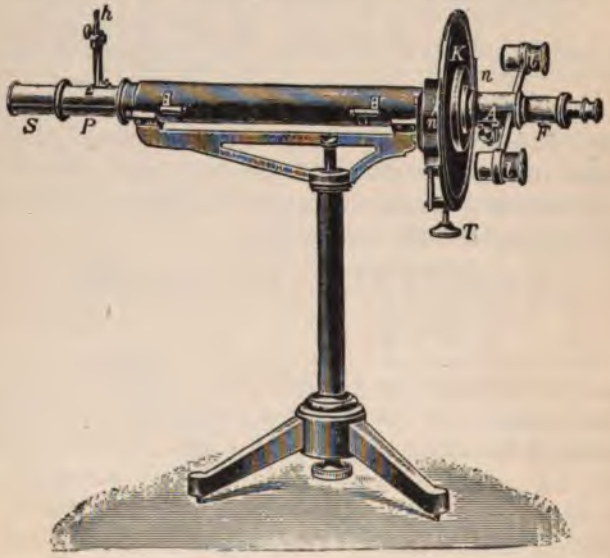


Fig. 29.

optical accessories have been added to the simple polarimeter described above to render the instrument more sensitive, but for these details the student must consult some special treatise.* The angle of rotation is dependent upon the nature of the liquid, the length of the column of substance through which the light passes, the wave-length of the light used, and the temperature at which the measurement is made. It is customary in polarimetric work to employ sodium light and, unless otherwise specified, it may be assumed that a given rotation corresponds to the D-line.

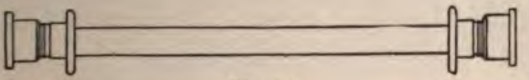


Fig. 30.

Specific and Molecular Rotation. The results of polarimetric measurements are expressed either as specific rotations or as molecular rotations, the latter being preferable since the optical activities of different substances may then be compared.

The specific rotation is obtained by dividing the observed rotation by the product of the length of the column of liquid and its density, or

$$[\alpha]_t = \frac{\alpha}{ld},$$

where $[\alpha]_t$ is the specific rotation at the temperature, t, α the observed angle, l, the length of the column of liquid in decimeters and d, its density. If the specific rotation is multiplied by the molecular weight of the substance, the molecular rotation is obtained, but owing to the fact that the resulting numbers are too large, it is customary to express the molecular rotation as one one-hundredth of this value, thus

$$[\alpha_M]_t = \frac{M\alpha}{100\,ld}.$$

The specific and molecular rotations of solutions of optically active substances may also be determined, if we assume that the solvent is without effect. While this assumption is justifiable with aqueous solutions, it is not so when non-aqueous solvents are used. If g grams of an optically active substance be dissolved in v cc. of solvent, then

---

* See for example, "The Optical Rotatory Power of Organic Substances and its Practical Applications." H. Landolt, trans. by J. H. Long.

$$[\alpha]_t = \frac{\alpha v}{lg}, \quad \text{and} \quad [\alpha_M]_t = \frac{M}{100} \cdot \frac{\alpha v}{lg},$$

or if the composition of the solution is expressed in terms of weight instead of volume, g grams of substance being dissolved in 100 grams of solution of density d, then

$$[\alpha]_t = \frac{100\,\alpha}{gdl}, \quad \text{and} \quad [\alpha_M]_t = \frac{M\alpha}{gdl}.$$

Optical Activity and Chemical Constitution. The fact that some substances have the power of rotating the plane of polarized light was first discovered by Biot, but the credit for recognizing the chemical significance of this fact belongs to Pasteur.* He discovered that ordinary recemic acid can be separated into two optically active modifications, one of which is dextro- and the other levo-rotatory, the numerical values of the two rotations being identical. If a solution of sodium ammonium racemate be allowed to evaporate at a low temperature, crystals of the composition $NaNH_4C_4H_4O_6 \cdot 4\,H_2O$ will separate. On close inspection it will be found that the crystals are not all alike, but that they may be divided into two classes, one class showing some unsymmetrical crystal surfaces which are oppositely placed in the crystals of the other class. The crystals of one class may

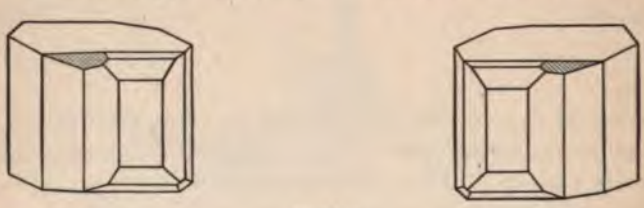


Fig. 31.

---

* Ann. Chim. Phys. (3), 24, 442 (1848); 28, 56 (1850); 31, 67 (1851).

be regarded as the mirror images of those of the other class: such crystals are said to be *enantiomorphous*. The forms usually assumed by the two enantiomorphous modifications of sodium ammonium reacemate are shown in Fig. 31. After separating the two forms Pasteur dissolved each in water, making the solutions of the same strength. The solution of the crystals with the "right-handed faces" was found to be dextro-rotatory, while that of the crystals with the "left-handed faces" was found to be levo-rotatory. Pasteur then decomposed the two salts obtained from sodium ammonium racemate and obtained the corresponding acids, which he called dextro- and levo-racemic acids. It was subsequently shown that the two acids were identical with dextro- and levo-tartaric acids. Finally, when Pasteur mixed equivalent amounts of concentrated solutions of dextro-and levo-tartaric acids, an appreciable evolution of heat was observed, indicating that a chemical reaction had taken place. After allowing the solution to stand for some time, crystals of ordinary racemic acid were obtained. Thus it was clearly proven that an optically inactive substance may be separated into two optically active modifications, possessing equal and opposite rotatory powers, and that by mixing equivalent quantities of the two optically active forms, the optically inactive substance may be recovered.

Pasteur discovered and applied three other methods in addition to the mechanical method already described, for the separation of a substance into its optically active modifications. These are as follows: — (a) *Method of Crystallization*; (b) *Method of Formation of Derivatives*; and (c) *Method of Ferments.*

Method of Crystallization. To a supersaturated solution of the racemic modification a very small crystal of one of the active forms is added. This will induce the separation of crystals of the same form, inoculation with a dextro-crystal producing the dextro-form and inoculation with a levo-crystal producing the levo-form.

Method of Formation of Derivatives. In this method an optically active substance, generally an alkaloid, is added to the racemic modification, producing optically active derivatives having different solubilities. Thus if cinchonine, an optically active alkaloid having the formula, $C_{19}H_{22}N_2O$, be added to the racemic modification of tartaric acid, the cinchonine salt of the levo-acid will crystallize first. The crystals of the cinchonine salt are then removed and after adding ammonia to displace the alkaloid, dilute sulphuric acid is added and the pure levo-tartaric acid is obtained.

Method of Ferments. Notwithstanding the fact that optical antipodes resemble each other so closely in most of their properties, Pasteur found that certain micro-organisms have the power of distinguishing sharply between these forms. For example, if *penicillium glaucum* be introduced into a solution of racemic tartaric acid, it thrives at the expense of the dextro-acid and eventually leaves the pure levo-form. In this method one of the active modifications is always lost.

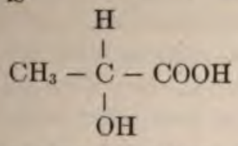
Pasteur was the first to point out that there must be some intimate connection between optical activity and the constitution of the molecule. It remained for Le Bel * and van't Hoff † to formulate independently and almost simultaneously an hypothesis to account for optical activity on the basis of molecular constitution. Their important work laid the foundation of spatial chemistry, commonly termed *stereochemistry* (derived from the Greek στερεός = a solid). Le Bel accepted Pasteur's view that optical activity is dependent upon a condition of asymmetry, but whether this asymmetry is a property of the crystal alone or whether it belongs to the molecule of the optically active substance, was the question he set himself to answer. He found, on dissolving certain optically active crystals in an inactive solvent, that the optical activity is imparted to the solution and therefore he concluded that the condition of asymmetry must exist in the chemical molecule. All of the optically active substances known to Le Bel were compounds of carbon. An examination of the formulas of these compounds led him to ascribe the cause of their optical activity to the presence of an *asymmetric* carbon atom, that is, a carbon atom combined with four different atoms or groups of atoms.

---

* Bull. Soc. Chim. (2), **22**, 337 (1874).

† Ibid. (2), **23**, 295 (1875).

One of the simplest examples is afforded by lactic acid, the structural formula of which is



$$CH_3 - \overset{\displaystyle H}{\overset{|}{\underset{\underset{\displaystyle OH}{|}}{C}}} - COOH$$

In this formula the asymmetric carbon atom is placed at the center and is in combination with hydrogen, hydroxyl, methyl and carboxyl. In connection with his work on the relation between optical activity and asymmetry, Le Bel pointed out that active forms never result from laboratory syntheses, the racemic modification being invariably obtained. Van't Hoff reached conclusions similar to those of Le Bel and proposed the additional theory of the *asymmetric tetrahedral carbon atom.* Since the four valences of the carbon atom are equivalent, as the work of Henry on methane has shown them to be, van't Hoff pointed out that the only possible geometrical arrangement of the atoms in the molecule of methane, must be that in which the carbon atom is placed at the center of a regular tetrahedron with the four hydrogen atoms at the four apices. He then pointed out that when the four valences of the tetrahedral carbon atom are satisfied with different atoms or groups, no plane of symmetry can be passed through the figure, the carbon atom being asymmetric. This conception of Le Bel and van't Hoff forms the basis of all stereochemistry, and has proved of inestimable value to the organic chemist in enabling him to explain the existence of many isomeric compounds. Thus, ordinary lactic acid can be split into

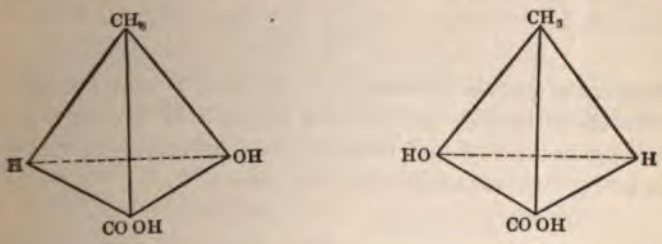
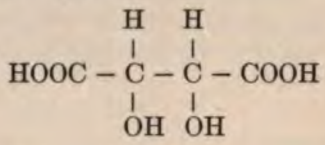


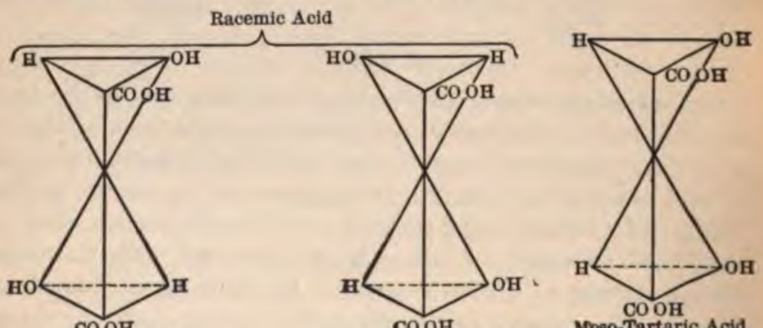
Fig. 32.

two optically active isomers. Aside from the fact that one acid is dextro- and the other is levo-rotatory, the properties of the two acids are practically identical. If the formulas are written spatially, the different groups can be arranged about the asymmetric carbon atom in such a way that the two tetrahedra shall be mirror images of each other, as shown in Fig. 32. It will be observed that these two tetrahedra can in no way be superposed so that the same groups fall over each other, that is to say, they are enantiomorphous forms. In tartaric acid there are two asymmetric carbon atoms as is evident when its structural formula is written as follows: —



$$\mathrm{HOOC} - \overset{\displaystyle H}{\underset{\displaystyle OH}{C}} - \overset{\displaystyle H}{\underset{\displaystyle OH}{C}} - \mathrm{COOH}$$

If the stereochemical formulas of the dextro- and levo-acids be represented as in Fig. 33, (a) and (b), it will be apparent that the theory admits of the existence of another isomer with the atoms and groups arranged as in Fig. 33 (c).



CO OH
d-Tartaric Acid
(*a*)

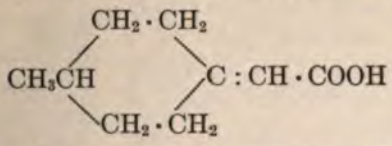
CO OH
l-Tartaric Acid
(*b*)

CO OH
Meso-Tartaric Acid
(*c*)

Fig. 33.

In this arrangement the asymmetry of the upper tetrahedron is the reverse of that of the lower, and consequently the optical activity of one-half of the molecule exactly compensates the optical activity of the other half, and the molecule as a whole is inactive. It is evident that such a tartaric acid could not be split into two active forms. Actually there are four tartaric acids known, viz., (1) inactive racemic acid which is separable into (2) dextro-tartaric acid and (3) levo-tartaric acid; and (4) meso-tartaric acid, an inactive substance which has never been separated into two active forms, but which has the same formula, the same molecular weight and in general the same properties as the dextro- or levo-tartaric acids. Inactive forms, such as meso-tartaric acid, are said to be inactive by *internal compensation.* This constitutes one of many beautiful confirmations of the van't Hoff theory of the asymmetric tetrahedral carbon atom.

Meso-tartaric acid furnishes an illustration of the fact that asymmetric carbon atoms may be present in the molecule without imparting optical activity to the substance. The converse of this proposition, however, that optical activity is dependent upon asymmetric carbon atoms, is generally true. Quite recently some substances apparently containing no asymmetric carbon atoms have been discovered which are optically active. An example of such a substance is 1-methyl cyclohexylidene-4 acetic acid, to which the following formula has been assigned: —



Other atoms aside from carbon may be asymmetric; thus certain compounds of nitrogen, sulphur and tin have been shown to be optically active. The theory also furnishes an explanation of the fact, pointed out by Le Bel, that optically active forms are never obtained by direct synthesis. Since the rotatory power is dependent upon the arrangement of the atoms and groups in the molecule, it follows from the doctrine of probability that as many dextro as levo configurations will be formed and consequently the racemic modification will be obtained. Up to the present time no satisfactory generalization has been discovered as to the factors determining the molecular rotation in any particular case. An attempt in this direction has been made by Guye,* in which he ascribes the magnitude of the observed rotation to the relative masses of the atoms or groups which are in combination with the tetrahedral carbon atom. But it cannot be mass alone which conditions optical activity, since substances are known which rotate the plane of polarization notwithstanding the fact that their molecules have two groups of equal mass in combination with the asymmetric carbon atom. The molecular rotations of the members of homologous series exhibit some regularities, but on the other hand many exceptions occur which cannot be satisfactorily explained. About all that can be said at the present time is, that optical activity is a constitutive property.

Magnetic Rotation. That many substances acquire the power of rotating the plane of polarized light when placed in an intense magnetic field was first observed by Faraday † in 1846.

The relation between chemical composition and magnetic rotatory power has since been investigated very exhaustively by W. H. Perkin,‡ his experiments in this field having been continued for more than fifteen years. In brief, Perkin's method of investigating magnetic rotatory power consisted in introducing the liquid to be examined into a polarimeter tube 1 decimeter in length and then placing the tube axially betweeen the perforated poles of a powerful electromagnet, as shown in Fig. 34. Upon exciting the magnet it was found that the plane of polarization had been rotated, either to the right or the left, the direction of rotation depending upon the direction of the current, the intensity of the magnetic field and the nature of the liquid. Perkin used the sodium flame as his source of light and carried out all of his experiments at 15° C. He expressed his results by means of the formula,

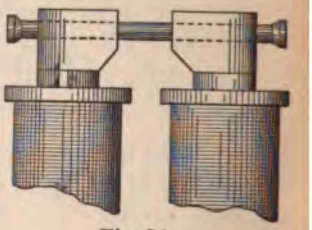


Fig. 34.

---

* Compt. rend., **110**, 714 (1890).

† Phil. Trans., **136**, 1 (1846).

‡ Jour. prakt. Chem. [2], **31**, 481 (1885); Jour. Chem. Soc., **49**, 777; **41**, 808; **53**, 561, 695; **59**, 981; **61**, 287, 800; **63**, 57; **65**, 402, 815; **67**, 255; **69**, 1025 (1886–1896).

$M\alpha/d$, α being the observed angle of rotation, d, the density of the liquid and M its molecular weight. All measurements were expressed in terms of water as a standard: thus if $M\alpha/d$ is the rotation for any substance and $M'\alpha'/d'$ is the corresponding rotation for water, then, according to Perkin, the *molecular magnetic rotation* will be given by the ratio, $M\alpha/d : M'\alpha'/d'$ or $M\alpha d'/M'\alpha' d$.

The molecular magnetic rotation for a large number of organic compounds has been determined by Perkin, who has shown it to be an additive property. In any one homologous series the value of the molecular magnetic rotation is given by the formula

$$\text{mol. mag. rotation} = a + nb,$$

where a is a constant characteristic of the series, b is a constant corresponding to a difference of CH_2 in composition, its value being 1.023, and n is the number of carbon atoms contained in the molecule. This formula is applicable only to compounds which are strictly homologous, isomeric substances in two different series having quite different rotations. The constitution of the molecule exerts as great an influence on magnetic rotation as it does on refraction, a double bond causing an appreciable increase in the value of a. The results of experiments on magnetic rotation show that nothing like the same regularities exist as have been discovered for molecular refraction and molecular volume. The rotatory powers of various inorganic substances have been determined, but the results are too irregular to admit of any satisfactory interpretation.

Absorption Spectra. When a beam of white light is passed through a colored liquid or solution and the emergent beam is examined with a spectroscope, a continuous spectrum crossed by a number of dark bands is obtained. A portion of the light has been absorbed by the liquid. Such a spectrum is known as an *absorption spectrum*. If instead of passing the light through a liquid it is passed through an incandescent gas, a spectrum will be obtained which is crossed by numerous fine lines, termed *Fraunhofer lines*. Such lines occupy the same positions as the corresponding colored lines in the emission spectrum of the gas.

It follows, therefore, that the absorption spectrum is quite as characteristic of a substance as its emission spectrum, and from a careful study of the absorption spectra of liquids we may expect to gain some insight into their molecular constitution. The pioneer workers in this field were Hartley and Baly * and it is largely to them that we owe our present experimental methods. The instrument employed for photographing spectra is called a *spectrograph,* a very satisfactory form being shown in Fig. 35. It differs from an ordinary spectroscope in that the eye-piece is replaced by a photographic camera. This attachment is clearly shown in the illustration. The plateholder is so constructed that only a narrow horizontal strip of the plate is exposed at any one time, thus making it possible to take a series of photographs on the same plate by simply lowering the holder. By means of a millimeter scale, also shown in the illustration, the plateholder can be moved through the same distance each time before expos-

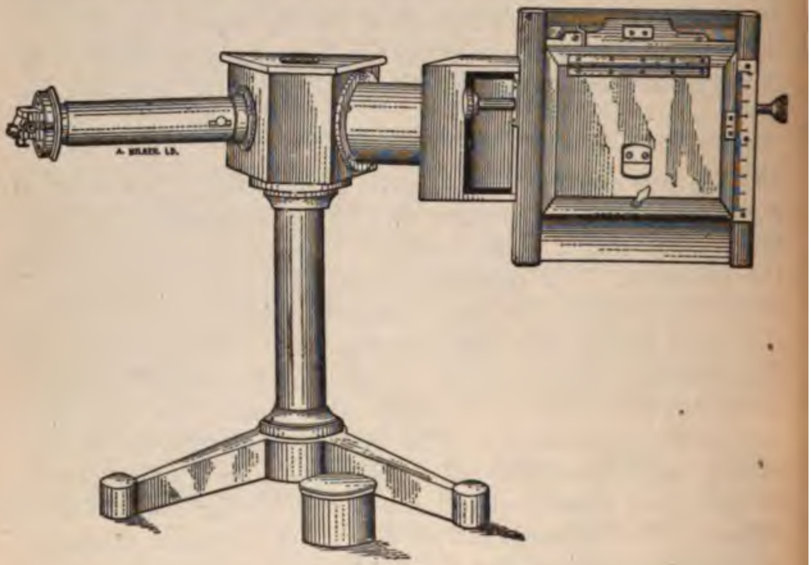


Fig. 35.

---

* See numerous papers in the Jour. Chem. Soc., since 1880.

ing a fresh portion of the plate, thus insuring an equally-spaced series of spectrum photographs. In order that spectra in the ultra-violet region may be photographed, it is customary to equip the instrument with quartz lenses and a quartz prism, ordinary glass not being transparent to the ultra-violet rays. Using a spectrograph furnished with a quartz optical system, it is possible to photograph on a single plate the entire spectrum from 2000 to 8000 Ångstrom units. A scale of wave-lengths photographed on glass is provided with the instrument so that the wave-lengths of lines or bands can be read off directly by laying the scale over the photographs.

The source of light to be used depends upon the character of the investigation. If a source rich in ultra-violet rays is desired, the light from the electric spark obtained between electrodes prepared from an alloy of cadmium, lead and tin is very satisfactory; or the light from an arc burning between iron electrodes may be used. For investigations in the visible region of the spectrum the Nernst lamp is unsurpassed. In using the spectrograph for the purpose of studying the constitution of a dissolved substance, it is necessary to determine not only the number and position of the absorption bands, but also the persistence of these bands as the solution is diluted.

According to Beer's law the product of the thickness, t, of an absorbing layer of solution of molecular concentration, m, is constant, or $mt = k$. If then the thickness of a given layer of solution is diminished n times, its absorption will be the same as that of a solution whose concentration is only $1/nth$ of that of the original solution. Thus, by varying the thickness of the absorbing layer we can produce the same effect as by changing the concentration. The convenient device of Baly for altering the length of the absorbing column of liquid is shown in Fig. 36 attached to the collimator of the spectrograph. It consists of two closely-fitting tubes, one end of each tube being closed by a plane, quartz disc. The outer tube is fitted with a small bulbed-funnel and is graduated in millimeters. The two tubes are joined by means of a piece of rubber tubing which prevents leakage of the contents, and at the same time admits of the adjustment of the column of liquid to the desired length by simply sliding the smaller tube in or out.

Molecular Vibration and Chemical Constitution. There are two systems of graphic representation of the results of spectroscopic investigations. In the first system, due to Hartley, the wave-lengths or their reciprocals, the frequencies, are plotted as abscissæ and the thicknesses of the absorbing layers, in millimeters, are plotted as ordinates. Such curves are known as *curves of molecular vibration*. The second system, due to Baly and Desch, is a modification of that developed by Hartley.

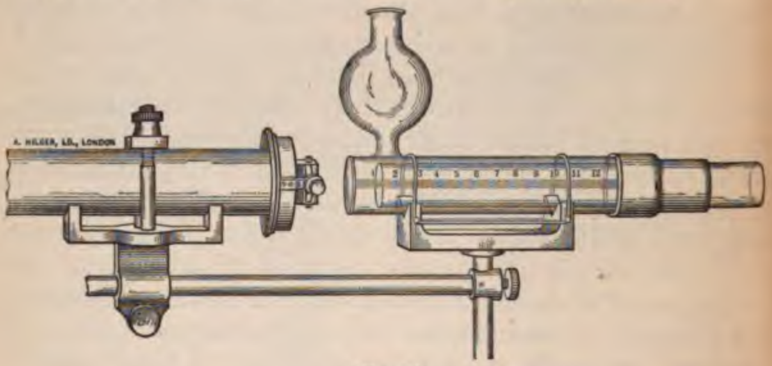
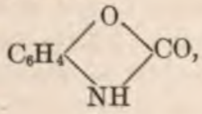
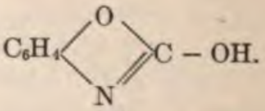


Fig. 36.

Baly and Desch suggested that for various reasons it would be more advantageous, if instead of plotting the thicknesses of the absorbing layers as ordinates, the logarithms of these thicknesses be plotted. Both methods have their advantages and both are used. As an illustration of the value of curves of molecular vibration in connection with questions of chemical constitution, we will take the case of o-hydroxy-carbanil. The constitution of this substance was known to be represented by one of the two following formulas: —



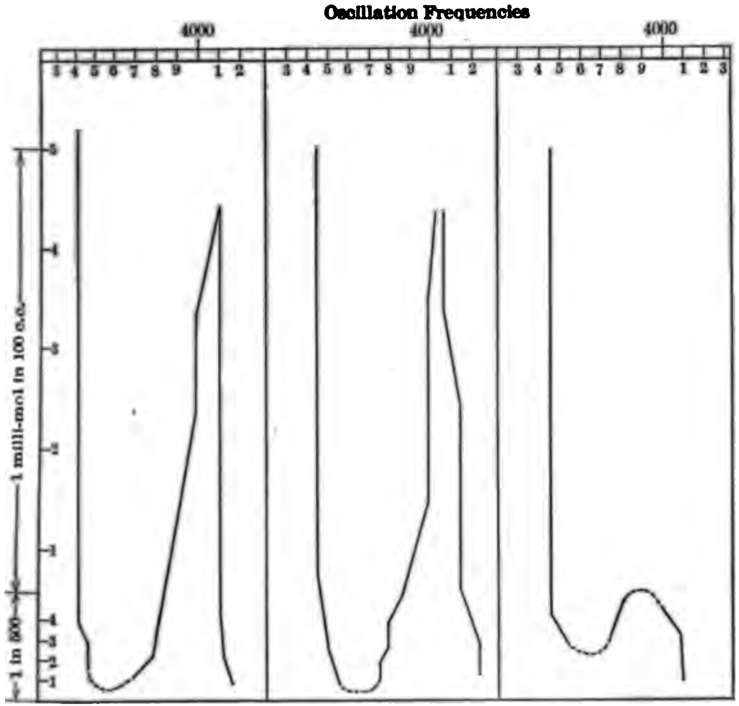
or



(a) (b)

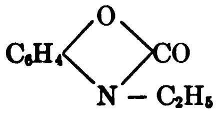
Hartley showed that the absorption spectra of the two ethyl derivatives, the lactam and lactim ethers, are very different.

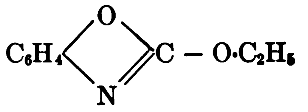
On comparing the curves of molecular vibration for the three substances (Fig. 37), it is apparent that the curves for the lactam ether and o-hydroxy-carbanil bear a close resemblance to each other, while the curve for the lactim ether is very different from the curves for the other two substances. The constitution of o-hydroxy-carbanil must then be very similar to that of the lactam ether. The formulas of the ethyl derivatives of the mother substance are known to be as follows: —



Lactam Ether O-Hydroxy-Carbanil Lactim Ether

Fig. 37.


Lactam ether


Lactim ether

Hartley concluded, therefore, that formula (a) represents the structure of the molecule of o-hydroxy-carbanil.

It is beyond the scope of this book to discuss at greater length the bearing of absorption spectra upon chemical constitution; but the student is earnestly advised to consult some book * treating of this important subject or to read some of the original papers.

Surface Tension. The attraction between the molecules of a liquid manifests itself near the surface where the molecules are subject to an unbalanced internal force. The condition of a liquid near its surface is roughly depicted in Fig. 38, where the dots *A*, *B*, and *C* represent molecules and the circles represent the spheres within which lie all of the other molecules which exert an appreciable attraction upon *A*, *B*, and *C*. The shaded portions represent those molecules whose attractions are unbalanced. These unbalanced forces will evidently tend to diminish the surface to a minimum value. That is, the contraction of the surface of a liquid involves the expenditure of energy by the liquid. The surface film of a liquid is consequently in a state of tension.

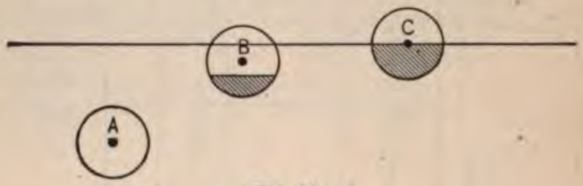


Fig. 38.

Some liquids wet the walls of a glass capillary tube while others do not. When the liquid wets the tube, the surface is concave and the liquid rises in the tube; on the other hand, when the liquid does not adhere, the surface is convex and the liquid is depressed in the tube. The law governing the elevation or depression of a liquid in a capillary tube was discovered by Jurin and may be stated thus: — *The elevation or depression of a liquid in a capillary tube is inversely proportional to the diameter of the tube.* Let Fig. 39 represent a capillary tube of radius r, immersed in a vessel of liquid whose density is d, and let the elevation of the liquid in the capillary be denoted by h. Then the weight of the column of liquid in the capillary will be $\pi r^2 hdg$, where g is the acceleration due to gravity. The force sustaining this weight is $2\pi r\gamma \cos\theta$, the vertical component, of the force due to the tension of the liquid surface at the walls of the tube, γ being the surface tension and θ the angle of contact of the liquid surface with the walls of the tube.

---

* Relation between Chem. Constitution and Phys. Properties. Samuel Smiles.

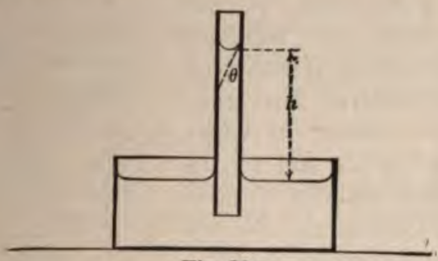


Fig. 39.

Therefore

$$\pi r^2 hdg = 2\pi r\gamma \cos\theta,$$

or

$$\gamma = \frac{hdgr}{2\cos\theta}.$$

In the case of water and many other liquids θ is so small that we may write $\theta = 0$, the foregoing expression becoming

$$\gamma = 1/2\, hdgr.$$

Thus the surface tension of a liquid can be calculated provided its density and the height to which it rises in a previously calibrated tube is known. When h and r are expressed in centimeters, γ will be expressed in dynes per centimeter or ergs per square centimeter. A simple form of apparatus for the determination of surface tension used by the author is shown in Fig. 40. A capillary tube, A, of uniform bore is sealed to a glass rod, E, which is held in position in the test tube, B, by means of a cork stopper. A short right-angled tube, D, and a thermometer, F, are also passed through the same cork stopper. The liquid whose surface tension is to be measured is introduced into the tube, *B*, the cork inserted and the tube placed inside of the larger tube, *C*, containing a liquid of known boiling-point. When the thermometer, *F*, has become stationary, the capillary elevation of the liquid is measured with a cathetometer. The tube, *D*, permits the escape of vapor from the liquid in *B* and at the same time insures equality of pressure inside and outside of the apparatus. The spiral tube, *G*, serves as an air condenser, preventing loss of vapor from the liquid in the outer tube. The surface tension of a liquid has been found to depend upon the nature of the liquid and also upon its temperature.

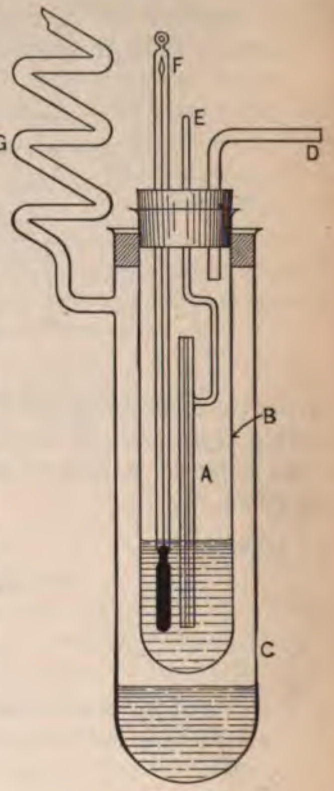


Fig. 40.

Surface Tension and Molecular Weight. In 1886, Eötvös * showed that the surface tension multiplied by the two-thirds power of the molecular weight and specific volume is a function of the absolute temperature, or

$$\gamma (Mv)^{\frac{2}{3}} = f(T),$$

where γ is the surface tension, M the molecular weight, v the specific volume or reciprocal of the density, and T the absolute temperature. Ramsay and Shields † modified the equation of Eötvös as follows: —

$$\gamma (Mv)^{\frac{2}{3}} = k(t_c - t - 6), \tag{1}$$

t_c being the critical temperature of the liquid, t the temperature of the experiment, and k a constant independent of the nature of the liquid. The physical significance of the two-thirds power of the molecular volume has been explained by Ostwald in the following manner: — Assuming the molecules to be spherical, we shall have for two different liquids, the proportion

---

* Wied. Ann., **27**, 448 (1886).

† Zeit. phys. Chem., **12**, 431 (1893).

$$V_1 : V_2 :: r_1^3 : r_2^3,$$

where V_1 and V_2 represent the volumes and r_1 and r_2 the radii of their respective molecules. Similarly the ratio of the surfaces, S_1 and S_2, of the molecules in terms of their respective radii, will be

$$S_1 : S_2 :: r_1^2 : r_2^2.$$

From these two proportions it follows that the ratio of the molecular surfaces in terms of the molecular volumes, will be

$$S_1 : S_2 :: V_1^{\frac{2}{3}} : V_2^{\frac{2}{3}}.$$

Making use of the value of M as determined in the gaseous state, Ramsay and Shields found the value of k for a large number of liquids to be equal to 2.12 ergs. Among the liquids for which this value of k was found were benzene, carbon tetrachloride, carbon disulphide and phosphorus trichloride. For certain other liquids such as water, methyl and ethyl alcohols and acetic acid, k was found to have values much smaller than 2.12. Ramsay and Shields attributed these abnormalities to an increase in molecular weight due to association, and suggested that the degree of association might be calculated from the equation

$$x^{\frac{2}{3}} = 2.12/k',$$

or

$$x = \left(\frac{2.12}{k'}\right)^{\frac{3}{2}}, \tag{2}$$

where x denotes the factor of association, and k' is the value of the constant for the associated liquid in equation (1). It was further pointed out by Ramsay and Shields that equation (1) affords a means of calculating the molecular weight of a pure liquid, provided we assume that for a non-associated liquid the mean value of k is 2.12. Since it is not an easy matter to determine the critical temperature with accuracy, Ramsay and Shields made use of a differential method, and thus eliminated t_c from equation (1). If the surface tension of a liquid be measured at two temperatures t_1 and t_2, and the corresponding densities are d_1 and d_2, we shall have

$$\gamma_1 (M/d_1)^{2/3} = k\,(t_c - t_1 - 6), \tag{3}$$

and

$$\gamma_2 (M/d_2)^{2/3} = k\,(t_c - t_2 - 6). \tag{4}$$

Subtracting equation (4) from equation (3), we obtain

$$\frac{\gamma_1 (M/d_1)^{2/3} - \gamma_2 (M/d_2)^{2/3}}{t_2 - t_1} = k = 2.12, \tag{5}$$

or solving equation (5) for M, we have

$$M = \left(\frac{k d_1^{2/3} \cdot d_2^{2/3} \cdot (t_2 - t_1)}{\gamma_1 d_2^{2/3} - \gamma_2 d_1^{2/3}}\right)^{3/2}.$$

The method of Ramsay and Shields is the best known method for the determination of the molecular weight of a pure liquid. If M is known to be the same in the liquid and gaseous states, or in other words, if k is independent of the temperature, even though its value is not exactly 2.12, the critical temperature of the liquid can be calculated by means of equation (1). In order that the correct value of the critical temperature may be obtained, Ramsay and Shields found it necessary to use the specific value of k for the liquid whose critical temperature is sought. As an illustration of the method of calculation, the following example is taken from the work of Ramsay and Shields.

For carbon disulphide,

γ at 19°.4 = 33.58 $\qquad$ γ at 46°.1 = 29.41

d at 19°.4 = 1.264 $\qquad$ d at 46°.1 = 1.223.

We have then for $\gamma\ (M/d)^{2/3}$, at the two temperatures,

$$(76/1.264)^{2/3} \times 33.58 = 515.4,$$

and

$$(76/1.223)^{2/3} \times 29.41 = 461.4.$$

Substituting in the equation

$$\frac{\gamma_1 (M/d_1)^{2/3} - \gamma_2 (M/d_2)^{2/3}}{t_2 - t_1} = k,$$

we have,

$$\frac{515.4 - 461.4}{46.1 - 19.4} = 2.022.$$

This value of k is so nearly equal to the mean value, 2.12, that we assume M to be the same in the liquid and gaseous states, and therefore we may substitute in equation (1) and calculate the critical temperature of carbon disulphide thus,

$$\gamma\,(M/d)^{\frac{2}{3}} = k\,(t_c - t - 6),$$

or solving for t_c, we have

$$t_c = \frac{\gamma(M/d)^{\frac{2}{3}}}{k} + t + 6.$$

Substituting the data given above, in the preceding equation, we obtain

$$t_c = 515.4/2.022 + 6 + 19.4,$$

or $$t_c = 280°.3\text{ C.}$$

Surface Tension and Drop-Weight. Morgan and his co-workers,* from measurements of the volumes of a single drop falling from the carefully-ground tip of a capillary tube, have shown that the weight of the falling drop, from such a tip can be used in place of the surface tension in the equation of Ramsay and Shields for the calculation of molecular weights and critical temperatures. The modified equation may be written thus: —

$$\frac{w_1\,(M/d_1)^{\frac{2}{3}} - w_2\,(M/d_2)^{\frac{2}{3}}}{t_2 - t_1} = k,$$

where w_1 amd w_2 are the respective weights of the falling drop at the temperatures, t_1 and t_2. The value of k obviously depends upon the tip employed.

The results obtained by the drop-weight method have been shown to be more trustworthy than those obtained by the method of capillary elevation. Morgan has further pointed out that when the experimental data are substituted in the preceding formula, the magnification of the experimental errors is appreciably greater than when use is made of the original formula,

$$w\,(M/d)^{\frac{2}{3}} = k\,(t_c - t - 6).$$

Morgan recommends therefore that this formula be used for the determination of molecular weights. After having calibrated a particular tip with pure benzene (a liquid which is known to be non-associated), and thus ascertaining the value of k, the drop-weights at several different temperatures are determined. If we assume M to have the same value in the liquid and gaseous states, the value of t_c can be computed by substituting the experimental data in the preceding equation. If at the different temperatures at which drop-weights are determined, the same value of t_c is obtained, then we may infer that the liquid is non-associated and, therefore, that the assumption made as to the value of M is confirmed. It is a singular fact that the calculated value of t_c for some liquids does not agree with the experimental value, although it remains constant throughout an extended range of temperatures. Morgan considers a constant value of t_c to be an indication of non-association, even if the value is fictitious. In this method the constancy of the calculated value of the critical temperature becomes the criterion of molecular association, and thus affords a means of determining whether the molecular weight in the liquid state is identical with that in the gaseous state. The values of t_c calculated from the drop-weights of an associated liquid become steadily smaller as the temperature increases. A large number of liquids have been studied by this method, and the results indicate that many of the substances which were considered to be associated by Ramsay and Shields are in reality non-associated; in fact, it appears from the work of Morgan that association is much less common among liquids than has hitherto been supposed.

---

* Jour. Am. Chem. Soc., 30, 360 (1908); 30, 1055 (1908).

Dielectric Constants. In 1837, Faraday discovered that the attraction or repulsion between two electric charges varies with the nature of the intervening medium or dielectric. If q_1 and q_2 represent two charges which are separated by a distance r, the force of attraction or repulsion, f, is given by the equation

$$f = \frac{1}{D} \cdot \frac{q_1 q_2}{r^2},$$

where D is a specific property of the medium known as the *dielectric constant*. The dielectric constant of air is taken as unity. Various methods have been devised for the experimental determination of the dielectric constant, but the scope of this book forbids even a brief description of the apparatus or an outline of the processes of measurement. For a description of these methods the student is referred to any one of the more complete physico-chemical laboratory manuals, or to the original communications of Nernst * and Drude.†

The values of the dielectric constants for some of the more common solvents are given in the accompanying table.

DIELECTRIC CONSTANTS AT 18° C.

Substance.	*D*
Hydrogen dioxide	92.8
Water	77.0
Formic acid	63.0
Methyl alcohol	33.7
Ethyl alcohol	25.9
Ammonia, liquid	22.0
Chloroform	5.0
Ether	4.4
Carbon disulphide	2.6
Benzene	2.3

The importance of this property of liquids will become more apparent in subsequent chapters, especially in those devoted to electrochemistry.

PROBLEMS.

1. It is desired to compare the molecular volumes of alcohol and ether. If the molecular volume of ether is determined at 20° C., at what temperature must the molecular volume of alcohol be determined? The boiling points of alcohol and ether are 78° and 35° respectively. *Ans.* 61° C.

2. A volume of 50 liters of air in passing through a liquid at 22° C. causes the evaporation of 5 grams of substance, the molecular weight of which is 100. What is the vapor pressure of the liquid in grams per square centimeter? *Ans.* 25.

---

* Zeit. phys. Chem., 14, 622 (1894).

† Ibid., 23, 267 (1897).

3. The boiling-point of ethyl propionate is 98°.7 C. and its heat of vaporization is 77.1 calories. Calculate its molecular weight.

4. The heat of vaporization of liquid ammonia at its boiling-point, under atmospheric pressure (– 33°.5 C.) is 341 calories. Is liquid ammonia associated?

5. Calculate the molecular volume of ethyl butyrate. The molecular volume determined by experiment is 149.1.

6. For propionic acid, $d = 1.0158$ and $n_D = 1.3953$. Calculate the molecular refraction by the formula of Lorenz-Lorentz and compare the value so obtained with that derived from the atomic refractions of the constituent elements.

7. The density of ether is 0.7208, of ethyl alcohol, 0.7935 and of a mixture of ether and alcohol containing p per cent of the latter, 0.7389. At 20° C. the refractive indices for sodium light are, for ether, 1.3536, for alcohol, 1.3619, and for the mixture, 1.3572. Calculate the value of p, using the Gladstone and Dale formula. *Ans.* 20.81.

8. At 20° C. the density of chloroform is 1.4823 and the refractive index for the D-line is 1.4472. Given the atomic refractivities of carbon and hydrogen, calculate that of chlorine, using the Lorenz-Lorentz formula. *Ans.* 5.999.

9. Calculate the surface tension of benzene in dynes per centimeter, the radius of the capillary tube being 0.01843 cm., the density of the liquid, 0.85, and the height to which it rises in the capillary, 3.213 cm. *Ans.* 24.71 dynes/cm.

10. Find the molecular weight of benzene, the surface tension at 46° C. being 24.71 dynes per centimeter, its critical temperature, 288°.5 C., its density, 0.85 and the value of $k = 2.12$. *Ans.* 77.7.

11. At 14°.8 C. acetyl chloride (density = 1.124) ascends to a height of 3.28 cm. in a capillary tube the radius of which is 0.01425 cm. At 46°.2 C. in the same tube the elevation is 2.85 cm. and the density = 1.064. Calculate the critical temperature of acetyl chloride. *Ans.* 234°.6 C.

12. From a certain tip the weights of a falling drop of benzene are 35.329 milligrams (temp. = 11°.4, density = 0.888) and 26.530 milligrams (temp. = 68°.5, density = 0.827). The molecular weight is the same in the liquid and gaseous states. Calculate the critical temperature of benzene. *Ans.* 286°.1 C.

CHAPTER VIII.

SOLIDS.

General Properties of Solids. Solids differ from gases and liquids in possessing definite, individual forms. Matter in the solid state is capable of resisting considerable shearing and tensile stresses. In terms of the kinetic theory of matter, the mutual attractive forces exerted by the molecules of solids must be regarded as superior to the attractive forces between the molecules of gases and liquids. With one or two exceptions all solids expand when heated, but there is no simple law expressing the relation between the increment of volume and the temperature. Rigidity is another characteristic property of solids, it being much more apparent in some than in others. Many solids are constantly undergoing a process of transformation into the gaseous state at their free surfaces, such a change being known as *sublimation*. Just as when a gas is sufficiently cooled it passes into the liquid state, so on cooling a liquid below a certain temperature, it passes into the solid state. The reverse transformations are also possible, a solid being liquefied when sufficiently heated, and the resulting liquid completely vaporized if the heating be continued. Heat energy is required to effect transition from the solid to the liquid state, just as heat energy is required to effect transition from the liquid to the gaseous state.

Obviously a substance in the solid state contains less energy than it does in the liquid state. The number of calories required to melt 1 gram of a solid substance is called its *heat of fusion*. It is often difficult to decide whether a substance should be classified as a solid or as a liquid. For example the behavior of certain amorphous substances such as pitch, amber and glass, is similar to that of a very viscous, inelastic liquid. Solids are generally classified as *crystalline* or *amorphous*. In crystalline solids the molecules are supposed to be arranged in some definite order, this arrangement manifesting itself in the crystal form. An amorphous solid on the other hand may be considered as a liquid possessing great viscosity and small elasticity. The physical properties of amorphous solids have the same values in all directions, whereas in crystalline solids the values of these properties may be different in different directions. When an amorphous solid is heated it gradually softens and eventually acquires the properties characteristic of a liquid, but during the process of heating there is no definite point of transition from the solid to the liquid state. On the other hand, when a crystalline solid is heated there is a sharp change from one state to the other at a definite temperature, this temperature being termed the *melting-point.*

Crystallography. The study of the definite geometrical forms assumed by crystalline solids is termed *crystallography.* The number of crystalline forms known is exceedingly large, but it is possible to reduce the many varieties to a few classes or systems by referring their principal elements — the planes — to definite lines called axes. These axes are so drawn within the crystal that the crystal surfaces are symmetrically arranged about them. This system of classification was proposed by Weiss in 1809. He showed that notwithstanding the multiplicity of crystal forms encountered in nature, it is possible to consider them as belonging to one of six systems of crystallization.

The six systems of Weiss are as follows: —

1. *The Regular System.* Three axes of equal length, intersecting each other at right angles (Fig. 41).

2. *The Tetragonal System.* Two axes of equal length and the third axis either longer or shorter, all three axes intersecting at right angles (Fig. 42).

3. *The Hexagonal System.* Three axes of equal length, all in the same plane and intersecting at angles of 60°, and a fourth axis, either longer or shorter and perpendicular to the plane of the other three (Fig. 43).

4. *The Rhombic System.* Three axes of unequal length, all intersecting each other at right angles (Fig. 44).

5. *The Monoclinic System.* Three axes of unequal length, two of which intersect at right angles, while the third axis is perpendicular to one and not to the other (Fig. 45).

6. *The Triclinic System.* Three axes of unequal length no two of which intersect at right angles (Fig. 46).

The position of a plane in space is determined by three points in a system of coördinates, and consequently the position of the face of a crystal is likewise determined by its points of intersection with the three axes, or by the distances from the origin of the system of coördinates at which the plane of the crystal face intersects the three axes. These distances are called the *parameters* of the plane.

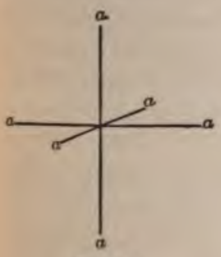


Fig. 41.

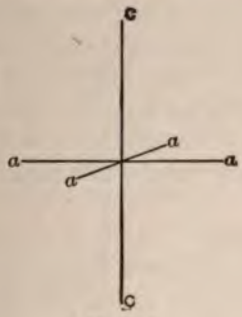


Fig. 42.

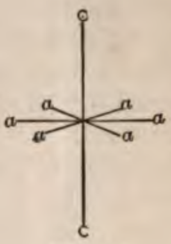


Fig. 43.

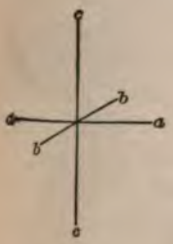


Fig. 44.

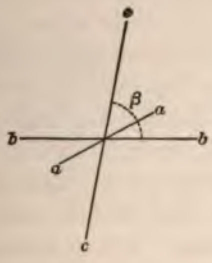


Fig. 45.

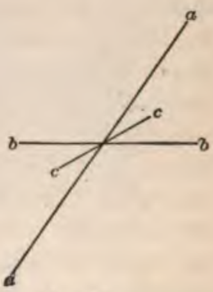


Fig. 46.

The fundamental law of crystallography discovered by Steno in 1669 may be stated thus: — *The angle between two given crystal faces is always the same for the same substance.* The fact that every crystalline substance is characterized by a constant interfacial angle, affords a valuable means of identification which is used by both chemists and mineralogists. The instrument employed for the measurement of the interfacial angles of crystals is called a *goniometer*. The crystal to be measured is mounted at the center of the graduated circular table of the goniometer, and the image of an illuminated slit, reflected from one surface of the crystal, is brought into coincidence with the cross-wires in the eyepiece of the telescope. The table is then turned until the image of the slit, reflected from the adjacent face of the crystal, coincides with the cross-wires. The interfacial angle of the crystal is determined by the number of degrees through which the table has been turned.

Properties of Crystals. The properties of all crystals, except those belonging to the regular system, exhibit differences dependent upon the direction in which the particular measurements are made. Thus the elasticity, the thermal and electrical conductivities, and in fact all of the physical properties of crystals which do not belong to the regular system, have different values in different directions. Crystals whose physical properties have the same values in all directions are termed *isotropic*, while those in which the values are dependent upon the direction in which the measurements are made, are called *anisotropic*. Crystals belonging to the regular system, and amorphous substances are isotropic. Certain amorphous substances, such as glass, which are normally isotropic, may become anisotropic when subjected to tension or compression. The phenomenon of double refraction observed in all crystals, except those belonging to the regular system, is due to their anisotropic character. Crystals belonging to the tetragonal and hexagonal systems resemble each other in one respect, viz.: that in all of them there is one direction, called the optic axis, or axis of double refraction (coincident with the principal crystallographic axis), along which a ray of light is singly refracted, while in all other directions it is doubly refracted. In crystals belonging to the rhombic, monoclinic, and triclinic systems, there are always two directions along which a ray of light is singly refracted. A crystal of Iceland spar ($CaCO_3$) affords a beautiful illustration of double refraction. On placing a rhomb of this substance over a piece of white paper on which there is an ink spot, two spots will be seen. On turning the crystal, one spot will remain stationary while the other spot will revolve about it. This property of Iceland spar is utilized in the construction of Nicol prisms for polariscopes.

The examination of sections of anisotropic crystals in a polariscope between crossed Nicol prisms, reveals something as to their crystal form. As has been stated, crystals of the tetragonal and hexagonal systems are *uniaxial*. If a section is cut from such a crystal perpendicular to the optic axis, and this is placed between the crossed Nicol prisms of a polariscope, in a convergent beam of white light, a dark cross and concentric, spectral-colored circles will be observed, Fig. 47. Upon turning the analyzer through 90° the colors of the circles will change to the respective complementary colors and the dark cross will become light. Crystals of the rhombic, monoclinic, and triclinic systems are *biaxial*. If a section of a biaxial crystal, cut perpendicular to the line bisecting the angle between the two axes, be placed in the polariscope and examined as in the preceding case, a series of concentric spectral-colored lemniscates surrounding two dark centers and pierced by dark, hyperbolic brushes, will be observed, as shown in Fig. 48. On rotating the analyzer, the colors will change to the corresponding complementary colors, as in the case of uniaxial crystals. The appearance of these figures is so varied and characteristic as to furnish, in many cases, a very satisfactory means of identifying anisotropic crystals.

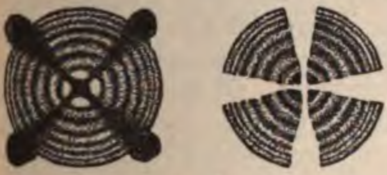


Fig. 46.

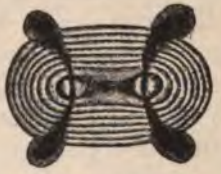


Fig. 47.

Etch Figures. The solubility of crystals has been shown to be different in different directions. Thus, if the surface of a crystalline substance be highly polished and then treated for a short time with a suitable solvent, faint patterns, known as *etch figures*, will appear as a result of the inequality of the rate of solution in different directions. When these figures are examined under the microscope the crystal-form can generally be determined. The examination of etch figures has come to be of prime importance to the metallographer. Thus, when an appropriate solvent is applied to the polished surface of an alloy, not only is the crystal form revealed by the etch figures, but also the presence of various chemical compounds may be recognized. By a careful study of the etch figures developed on the surface of highly polished steel, the metallographer may gather important information as to its previous history, especially its heat treatment.

Crystal Form and Chemical Composition. From the preceding paragraphs it might be inferred that the same substance always assumes the same crystal form. While this is true in general, there are some substances which appear in several different crystal forms. This phenomenon is termed *polymorphism.*

Calcium carbonate is an example of a substance crystallizing in more than one form. As calcite, it crystallizes in the hexagonal system, while as aragonite, it crystallizes in the rhombic system. Such a substance is said to be *dimorphous*. Of the several factors controlling polymorphism, temperature is the most important. Thus sulphur crystallizes at temperatures above 95°.6 in the monoclinic system, while at lower temperatures it assumes the rhombic form. The temperature at which it changes from one form into the other is termed its *transition temperature*. As has been mentioned in an earlier chapter (p. 14), some substances may crystallize in the same form, the characteristic interfacial angles being nearly identical. Such substances are said to be *isomorphous*. This phenomenon, discovered by Mitscherlich, has been of great use in connection with the earlier investigations on atomic weights, as has already been pointed out.

There can be little doubt as to the existence of an intimate connection between crystalline form and chemical composition. Ever since the early part of the nineteenth century, when Haüy established the science of crystallography, various attempts have been made by chemists and crystallographers to connect crystalline form with chemical constitution. In 1906, Barlow and Pope * made a most notable contribution to the theories concerning the relation between crystalline form and chemical constitution. Their ideas may be summarized as follows: — If each atom be considered as appropriating a certain space, called its sphere of atomic influence, then (1) *the spheres of atomic influence are so arranged as to occupy the smallest possible volume in every crystal;* (2) *the volumes of the spheres of atomic influence in any substance are proportional to the valences of the constituent atoms;* (3) *the volumes of the spheres of influence of the atoms of different elements of the same valence are nearly equal, any variation being in harmony with their relations in the periodic system.* Barlow and Pope have shown that the general agreement between theory and observation is most satisfactory, a particularly strong argument in favor of this theory being the very plausible explanation which it furnishes for a large number of crystallographic facts. It is without doubt the best working hypothesis which has yet been offered for the investigation of the dependence of crystalline form upon a definite chemical constitution.

Compressibilities of the Solid Elements. A series of careful measurements of the compressibilities of the elements by T. W. Richards and his collaborators,† has revealed the fact that compressibility is a periodic function of atomic weight. Richards has advanced some interesting suggestions as to the importance of compressibility in connection with intermolecular cohesion and atomic volume. In fact, Richards' theory of compressible atoms may be regarded as a valuable supplement to the theory of Barlow and Pope and, taken together, these two theories constitute a rational basis for the science of chemical crystallography.

X-Rays and Crystal Structure. In 1912, Laue pointed out that the regularly arranged atoms or molecules of a crystal should act as a three-dimensional diffraction grating toward the X-rays. He showed mathematically that on traversing a thin section of a crystal, a pencil of X-rays should give rise to a diffraction pattern arranged symmetrically round the primary beam as a center. A photographic plate placed perpendicular to the path of the rays and behind the crystal should reveal, on development, a central spot due to the action of the primary rays, and a series of symmetrically grouped spots due to the diffracted rays.

---

* Jour. Chem. Soc., **91**, 1150 (1907).

† Zeit. phys. Chem., **61**, 77, 100, 171, 183 (1908).

Laue's predictions were verified experimentally by Friedrich and Knipping, who obtained numerous plates showing a variety of geometrical patterns corresponding to the structural differences of the crystals examined. The analysis of the Laue diffraction patterns, while furnishing valuable information as to the internal structure of crystals, is nevertheless extremely complex.

W. H. Bragg and his son W. L. Bragg * have devised an X-ray spectrometer in which use is made of the fact that the regularly spaced atoms of a crystal reflect the X-rays in much the same way that light is reflected (diffracted) by a plane grating. By observing the angles of reflection from the different faces of a crystal for an incident radiation of known wave-length, it is an easy matter to calculate the distances between the atoms of the crystal which function as diffraction centers.

By means of the X-ray spectrometer the internal structure of a number of crystals has been determined. One of the most interesting results to the chemist is that obtained with the diamond. The X-ray spectra of the diamond reveal the fact that each carbon atom is situated at the center of a regular tetrahedron formed by four other carbon atoms.

In commenting on this method of studying crystal structure, W. H. Bragg says: — "Instead of guessing the internal arrangement of the atoms from the outward form assumed by the crystal, we find ourselves able to measure the actual distances from atom to atom and to draw a diagram as if we were making a plan of a building."

---

* See "X-Rays and Crystal Structure" by W. H. Bragg and W. L. Bragg.

Heat Capacity of Solids. Recent investigations of specific heats of solids at extremely low temperatures have resulted in the formulation of several interesting relationships between heat capacity and temperature.

At ordinary temperatures the molecules of a crystalline solid may be assumed to be in a state of violent, unordered motion. As the temperature is lowered, the amplitude of the molecular oscillations steadily diminishes until finally, at the absolute zero, there is in all probability a complete cessation of motion. In the neighborhood of the absolute zero, where the amplitude of the molecular oscillations is negligible, a crystalline solid may be assumed to possess the properties characteristic of a perfectly elastic body. In other words, the crystalline forces holding the molecules together would preponderate over the feeble thermal forces tending to initiate molecular oscillations within the solid. Under these conditions the solid as a whole would exhibit the same behavior as a single molecule, that is to say, the solid would function as a perfectly elastic body.

On this assumption Debye * has derived the following equation expressing the heat capacity of a solid, C_v, in terms of its absolute temperature T,

$$C_v = 71.9\frac{T^3}{\theta^3}\cdot$$

In this equation θ is a constant characteristic of each solid and has the same dimensions as T. The value of θ varies between the limits $\theta = 50$ for calcium and $\theta = 1840$ for carbon. The agreement between the observed and calculated values of C_v has been found to be excellent up to $T = \theta/12$.

When this latter temperature is exceeded, the molecules of the solid begin to absorb more and more heat energy and to vibrate independently about their centers of oscillation. The failure of Debye's equation is to be expected under these conditions since the solid is no longer behaving as one large molecule. Obviously the lighter the molecules and the greater the crystalline forces within the solid, the higher must the temperature become before the individual molecules can acquire appreciable kinetic energy. This is apparent from the familiar dynamical principle, that the kinetic energy of a vibrating particle is proportional to its mass and to the square of its vibration frequency. In the case of lead, which is a soft, malleable solid with a relatively low melting point, it is reasonable to infer that the crystalline forces are feeble, and consequently we should expect that molecular and atomic vibrations would be set up at quite low temperatures. Furthermore, since the atoms of lead are extremely heavy, their kinetic energy must be great. The correctness of these conclusions is confirmed by the fact that the Debye equation when applied to lead has been found to hold only over a very short range of temperature. On the other hand, the equation has been found to hold for the diamond up to a temperature of about 200° absolute. In this case we have a solid in which the crystalline forces are extremely powerful and in which the atoms are relatively light. A fairly high temperature must be attained before the energy absorbed by the individual atoms of the diamond acquires appreciable magnitude.

---

* Ann. Physik., **39**, 789 (1912).

The absorption of energy by the vibrating molecules continues to increase as the temperature is raised until ultimately, at the melting point of the solid, the crystalline forces become negligible. As this temperature is approached therefore, the intermolecular restraint becomes less and less and the mean kinetic energy of the molecules approaches that of the molecules of the molten solid.

As has already been stated in Chapter I (p. 11), Dulong and Petit, in 1819, discovered the interesting fact that the atomic heats of the solid elements have a constant value of 6.5. The importance of this generalization in connection with the verification of atomic weights has already been pointed out. Quite recently, Lewis * has directed attention to the fact that it is much more rational to calculate the atomic heat of an element from the specific heat at constant volume rather than from the specific heat at constant pressure. While it is impossible to measure the specific heat at constant volume, its value may be derived from the specific heat

---

* Jour. Am. Chem. Soc., **29**, 1165 (1907).

at constant pressure by an application of the laws of thermodynamics. Thus, Lewis has obtained the formula

$$C_p - C_v = \frac{T\alpha^2 V}{41.78\,\beta},$$

where T denotes the absolute temperature, α the coefficient of expansion, β the coefficient of compressibility, C_p and C_v the atomic specific heats at constant pressure and constant volume respectively and V the atomic volume. By means of this equation, Lewis has established the following generalization: — *Within the limits of experimental error, the atomic heat at constant volume, at* 20° C., *is the same for all solid elements whose atomic weights are greater than that of potassium, and is equal to 5.9.* In the case of a solid having a high melting point, the violent agitation of its constituent molecules and atoms as the temperature is raised, will undoubtedly produce a corresponding increase in the amplitude of vibration of its electrons together with an increase in their translational velocity among the molecules. Under these conditions, the specific heat at constant volume should be greater than 5.9 calories. This conclusion cannot be verified experimentally until the values of α and β in the foregoing equation have been determined at high temperatures.

The complete heat capacity curves for three typical solid elements, lead, aluminium, and carbon, are given in Fig. 49. It is apparent from these curves that the absorption of heat energy by a crystalline solid may be considered as taking place in three distinct stages, as follows: — (1) In the neighborhood of the absolute zero, the heat capacity remains practically zero; (2) the heat capacity increases rapidly with the temperature; and (3) the heat capacity increases slowly, approaching asymptotically the limiting value 5.9 for $T = \infty$. For a malleable, low melting element of high atomic weight, such as lead, the first two stages are very short and the final stage commences at a low temperature. On the contrary, with a hard, high melting element of low atomic weight, such as carbon in the form of diamond, the final stage is not reached at any temperature within the range covered by the experiments.

The Nernst-Lindemann Equation. Recently, several equations have been derived expressing the heat capacity of a solid in terms of temperature and arbitrary constants. All of these equations are based upon the so-called "quantum theory" according to which the absorption of heat energy by matter is supposed to take place in a discontinuous manner, the discrete units of energy being termed *quanta*. While the discussion of the quantum theory and the equations connecting heat capacity and temperature lies outside of the scope of this book, mention should nevertheless be made of the empirical equation derived by Nernst and Lindemann.* This equation gives values of C_v which are in remarkably close agreement with the values determined by direct experiment. The equation may be written in the following form:—

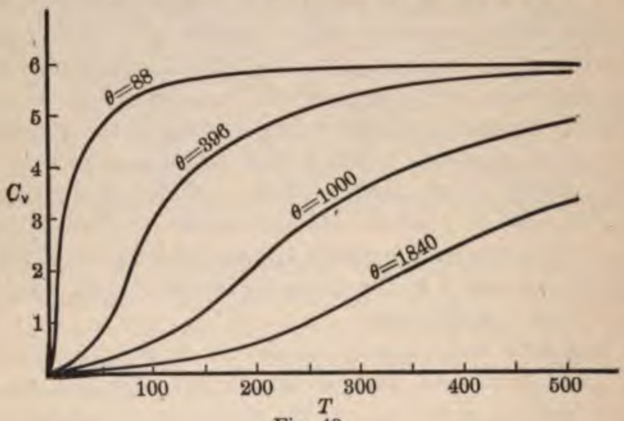


Fig. 49.

$$C_v = \frac{3}{2}R\left[\frac{\left(\frac{\theta}{T}\right)^2 e^{\frac{\theta}{T}}}{(e^{\frac{\theta}{T}}-1)^2} + \frac{\left(\frac{\theta}{2T}\right)^2 e^{\frac{\theta}{2T}}}{(e^{\frac{\theta}{2T}}-1)^2}\right].$$

In this expression, R is the molecular gas constant $R = 2$ calories, e is the base of the natural system of logarithms and θ is a constant depending upon the nature of the solid.

---

* Zeit. Elektrochem., 17, 817 (1911).

The value of θ may be calculated with a fair degree of accuracy by means of the equation

$$\theta = 136\left(\frac{T_f}{A}\right)^{\frac{1}{2}}\left(\frac{d}{A}\right)^{\frac{1}{3}},$$

in which T_f denotes the absolute melting point of the substance, A its atomic weight and d its density.

Liquid Crystals. In addition to possessing well-defined geometrical forms, crystalline substances are characterized by their resistance to deformation when subjected to mechanical stress, and by the property of melting sharply at definite temperatures with the production of transparent liquids.

In 1888, two substances, cholesteryl acetate and cholesteryl benzoate, were found by Reinitzer * to behave in an anomalous manner when heated. At definite temperatures these substances melted to turbid liquids which, in turn, became clear on further heating, the latter change also taking place at definite temperatures. On cooling the clear liquids, the reverse series of changes was found to occur.

Examination of the turbid liquids revealed the fact that they resembled ordinary liquids in their general behavior, such as assuming the spherical shape when suspended in a medium of the same density, or of rising in a capillary tube under the influence of surface tension. But in addition to possessing the properties characteristic of the liquid state, Lehmann discovered that they possessed optical properties which had hitherto been observed only with solid, crystalline substances. Their behavior towards polarized light was such as to warrant the conclusion that these turbid liquids are anisotropic. In view of these facts, Lehmann proposed that liquids possessing these properties should be called *liquid crystals*, the term implying that under ordinary conditions, the crystalline forces in these substances are so feeble that the crystals readily undergo deformation and actually flow like liquids. That these turbid liquids are not emulsions, is proven by the fact that when they are examined under the microscope, the turbidity is found to be due to the aggregation of a myriad of differently oriented transparent crystals. All subsequent investigation of liquid crystals has failed to show any lack of homogeneity.

---

* Monatshefte, 9, 435 (1888).

The number of such substances known at the present time is fairly large.

CHAPTER IX.

SOLUTIONS.

Classification of Solutions. Having dealt with the properties of pure substances in the gaseous, liquid and solid states we now proceed to the consideration of the properties of mixtures of two or more pure substances. When such a mixture is chemically and physically homogeneous, and no abrupt change in its properties results from an alteration of the proportions of the components of the mixture, it is termed a *solution*. When one substance is dissolved in another, it is customary to designate as the *solvent* that component which is present in the larger proportion, the other component being termed the *solute*. When not more than one-tenth mol of solute is present in one liter of solution, the solution is said to be *dilute*. The detailed study of dilute solutions will be deferred until the next chapter.

There are nine possible classes of solutions, as follows: —

(1) Solution of gas in gas;
(2) Solution of liquid in gas;
(3) Solution of solid in gas;
(4) Solution of gas in liquid;
(5) Solution of liquid in liquid;
(6) Solution of solid in liquid;
(7) Solution of gas in solid;
(8) Solution of liquid in solid;
(9) Solution of solid in solid.

While examples of all of these different types of solutions are known, only the more important classes will be considered here.

Solutions of Gases in Gases. In solutions of this class the components may be present in any proportions, since gases are completely miscible. In a mixture of gases where no chemical action occurs, each gas behaves independently, the properties of the gaseous mixture being the sum of the properties of th stituents. Thus, *the total pressure of a mixture of several g equal to the sum of the pressures which each gas would exert alone present in the volume occupied by the mixture.* This la discovered by Dalton * and is known as *Dalton's law of pressures.* If the partial pressures of the constituent ga denoted by p_1, p_2, p_3, etc., and P and V represent the total sure and the total volume of the gaseous mixture, then

$$PV = V (p_1 + p_2 + p_3 + \ . \ . \ . \ ).$$

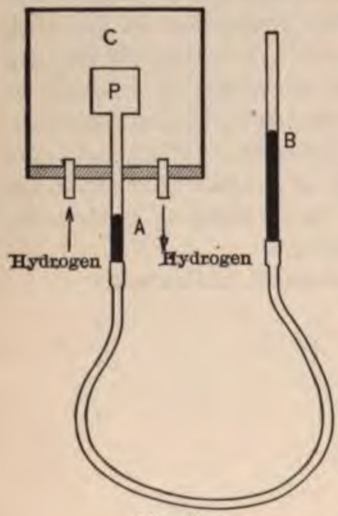


Fig. 50.

Dalton's law holds when the partial pressures are not too its order of validity being the as that of the other gas laws. ton's law can be tested expe tally by comparing the total pr of the gases with the sum of th sures exerted by each gas mixture. Van't Hoff pointe the possibility of measuring th tial pressure of one of the tw ponents of a gas mixture, pr a diaphragm could be found would be pervious to one gases but not to the other. shown shortly afterward by say,† that the walls of a ve palladium, when sufficiently h permit the free passage of hy but not of nitrogen. The wa said to be *semi-permeable.* A sketch of the apparatus u Ramsay in the verification of Dalton's law is shown in F A small vessel of palladium, P, containing nitrogen, is con with a manometer AB, which serves to measure the pressure gas in P. The vessel P is enclosed within a larger vessel C, can be filled with hydrogen at known pressure. On heating passing a current of hydrogen at a definite pressure through C, the hydrogen enters P until the pressures due to hydrogen inside and outside are equal. The total pressure in P, measured on the manometer, is greater than the pressure in C. The difference between the two pressures is very nearly equal to the partial pressure of the nitrogen. Conversely, if a mixture of the two gases be introduced into P, which is then heated and maintained at sufficiently high temperature to insure its permeability to hydrogen, the partial pressure of the nitrogen can be determined by passing a current of hydrogen at known pressure through C until equilibrium is attained, as shown by the manometer. The difference between the external and internal pressures is the partial pressure of the nitrogen. This experiment has a very important bearing upon the modern theory of solution.

---

* Gilb. Ann., 12, 385 (1802).

† Phil. Mag. (5), 38, 206 (1894).

Solutions of Gases in Liquids. The solubility of gases in liquids is limited, the extent to which they dissolve depending upon the pressure, the temperature, the nature of the gas, and the nature of the solvent. When a liquid cannot absorb any more of a gas at a definite temperature, it is said to be *saturated*, and the solution is called a *saturated solution*. The solubility of a gas in a liquid is defined by Ostwald as the ratio of the volume of the gas absorbed to the volume of the absorbing liquid at a specified temperature and pressure, or if the solubility of the gas be represented by S, we have

$$S = v/V,$$

where v is the volume of gas absorbed and V is the volume of the absorbing liquid. The "absorption coefficient" of Bunsen in terms of which he expressed the results of his measurements of the solubility of gases, may be defined as the volume of a gas, reduced to 0° C. and 76 cm. pressure which is absorbed by unit volume of a liquid at a certain temperature and under a pressure of 76 cm. of mercury. In certain cases the volume of the gas absorbed is found to be independent of the pressure, so that if α is the coefficient of gaseous expansion, and β Bunsen's coefficient of absorption, then

$$S = \beta\,(1 + \alpha t).$$

The solubilities of a few gases in water and alcohol as determined by Bunsen are given in the following table: —

Gas.	Water.		Alcohol.	
	0°	15°	0°	15°
Hydrogen	0.0215	0.0190	0.0693	0.0673
Oxygen	0.0489	0.0342	0.2337	0.2232
Carbon dioxide	1.797	0.1002	4.330	3.199

The solubility of gases in water is appreciably diminished by the presence of dissolved solids or liquids, especially electrolytes. Various theories have been proposed to account for the diminished solubility of gases in salt solutions but the most satisfactory is that due to Philip,* who suggests that the phenomenon is caused by the hydration of the dissolved salt. A portion of the water in the salt solution is supposed to be in combination with the salt, the water which is thus removed from the role of solvent, being no longer free to absorb gas. The solubility of a gas increases with increase in pressure. For gases which do not react chemically with the solvent, there exists a simple relation between pressure and solubility, discovered by Henry.† This relation, known as *Henry's law* may be stated as follows: — *When a gas is absorbed in a liquid, the weight dissolved is proportional to the pressure of the gas.* Since pressure and volume, at constant temperature, are inversely proportional (Boyle's law), the law of Henry may be stated thus: — *The volume of a gas absorbed by a given volume of liquid is independent of the pressure.* There is yet another form in which the law may be stated which is instructive in connection with the modern theory of solution. When a definite volume of liquid is saturated with a gas at constant temperature and pressure, a condition of equilibrium is established between the gas in solution and that in the free space over the solution, therefore, Henry's law may be stated as follows: — *The concentration of the dissolved gas is directly proportional to that in the free space above*

---

* Trans. Faraday Soc., 3, 140 (1907).

† Gilb. Ann., 20, 147 (1805).

the liquid. If c_1 represents the concentration of the gas in the liquid and c_2 the concentration in the free space above the liquid, Henry's law may be expressed thus: —

$$c_1/c_2 = k,$$

where k is known as the *solubility coefficient.*

Dalton showed that the solubility of the individual gases in a mixture of gases is directly proportional to their partial pressures, the solubility of each gas being nearly independent of the presence of the others.

As will be seen from the foregoing table, the solubility of a gas in a liquid diminishes with increase in temperature. Concerning the influence of the nature of the gas on its solubility, it may be said that those gases which exhibit acid or basic reactions are the most soluble, the solubilities of neutral gases being small. In the case of many of the very soluble gases Henry's law does not hold. For example, ammonia, a gas having marked basic properties and a large coefficient of solubility, does not obey Henry's law at ordinary temperatures, the mass of ammonia absorbed not being proportional to the pressure. The curve showing the variation in solubility with pressure at 0° C. has two marked discontinuities. At temperatures above 100° C. the gas obeys Henry's law. Sulphur dioxide behaves similarly, the law holding only for temperatures exceeding 40° C.

With regard to the connection between the solvent power of a liquid and its nature but little is known. About all that can be said is, that the order of solubility of gases in different liquids is the same. Thus in the preceding table the solubilities of hydrogen, oxygen and carbon dioxide in water and in alcohol will be seen to be approximately proportional. A slight change in volume always results when a gas is dissolved in a liquid. In general it may be said that the less compressible a gas is, the greater is the increase in volume produced when it is absorbed by a liquid. It is of interest to note that the increase in volume caused by the solution of a gas is nearly equal to the value of b for the gas in the equation of van der Waals. This is shown in the following table: —

Gas.	Increase in Vol.	b
Oxygen	0.00115	0.000890
Nitrogen	0.00145	0.001359
Hydrogen	0.00106	0.000887
Carbon dioxide	0.00125	0.000866

Solutions of Liquids in Liquids. Solutions of liquids in liquids can be divided into three classes as follows: — (1) Liquids which are miscible in all proportions; (2) Liquids which are partially miscible; and (3) Liquids which are immiscible. Examples of these three classes in the order mentioned are, alcohol and water, ether and water, and benzene and water. As to the cause of miscibility and non-miscibility of liquids very little is known.

Partial Miscibility. If a small amount of ether is added to a large volume of water in a separatory funnel and the mixture vigorously shaken, a perfectly homogeneous solution will be obtained. On gradually increasing the amount of ether, shaking after each addition, a concentration will eventually be reached at which a separation into two layers will take place. The upper layer is a saturated solution of water in ether and the lower layer is a saturated solution of ether in water. So long as the relative amounts of the two liquids is such that the mixture does not become homogeneous on standing, the composition of the two layers will be independent of the relative amounts of the two components. Measurements of the mutual solubility of liquids have been made by Alexieeff * by placing weighed amounts in sealed tubes and observing the temperature at which the mixture became homogeneous. In general the solubility of a pair of partially miscible liquids increases with the temperature, and therefore it may be inferred that at a sufficiently high temperature the mixture will become perfectly homogeneous. An example of this type of binary mixture is furnished by phenol and water, the solubility curve of which is shown in Fig. 51. In this diagram temperature is plotted on the axis of ordinates and percentage composition of the solution on the axis of abscissæ. Starting

* Jour. prakt. Chem., **133**, 518 (1882); Bull. Soc. Chem., **38**, 145 (1882).

with a small amount of phenol and adding it in increasing quantities to a large volume of water, a concentration will eventually be reached at which the solution will separate into two layers. This concentration is represented by the point *A*. On raising the

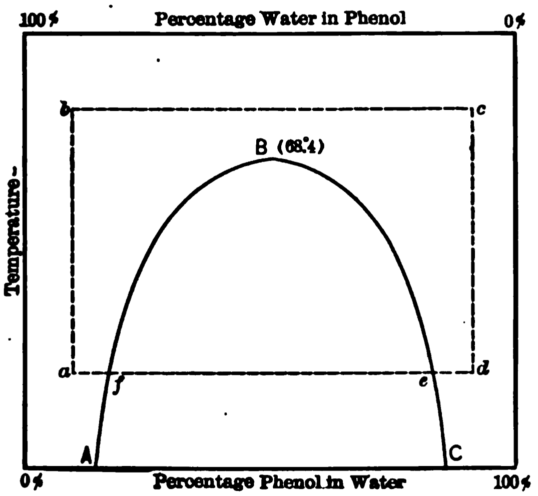


Fig. 51.

temperature, the solubility of phenol in water increases, as shown by the curve *AB*. In like manner, starting with pure phenol and adding increasing amounts of water, separation into two layers will occur at a concentration represented by the point *C*. As the temperature is raised the solubility of water in phenol increases, as shown by the curve *CB*. When the temperature is raised above 68°.4 C., corresponding to the point *B*, phenol and water become miscible in all proportions.

If we start with a solution whose temperature and composition is represented by the point *a*, the addition of increasing amounts of phenol, at constant temperature will be represented by the dotted line *afed*. When the point *f* is reached, the solution will separate into two layers the composition of which will be independent of the relative amounts of phenol and water. At *e* the solution will again become homogeneous. If the solution represented by the point *a* be again chosen as the starting point, and its composition be kept unaltered while the temperature is raised to a value above 68°.4 C., the change will be represented by the dotted line *ab*. If now the temperature be maintained constant and the percentage of phenol increased, the alteration in composition will be effected without discontinuity, as represented by the dotted line *bc*. On cooling the solution represented by the point *c* to the initial temperature of *a*, the point *d* will be reached. Thus it is possible to pass from *a* to *d* by the path *abcd* without causing a separation of the components into two layers. There is an analogy between the solubility curve of a pair of partially miscible liquids and the dotted, parabolic curve in the diagram of the isothermals of carbon dioxide, shown in Fig. 23. In both cases there is but one phase outside of the curves, while two phases are coexistent within the area enclosed by the curves. The analogy may be traced further, since in each case only one phase can exist above a certain temperature. The temperature corresponding to the apex of the parabolic curve in Fig. 23, is termed the critical temperature of carbon dioxide and by analogy the temperature corresponding to the point, *B*, in Fig. 51 is called the *critical solution temperature*. The mutual solubilities of some pairs of partially miscible liquids were found by Alexieeff to diminish with increasing temperature. Thus a mixture of ether and water, which is perfectly homogeneous at ordinary temperatures, becomes turbid on warming. A specially interesting pair of liquids is nicotine and water. At ordinary temperatures these liquids are miscible in all proportions. If the temperature is raised above 60° C., the solution becomes turbid owing to incomplete miscibility. On continuing to heat the mixture the mutual solubility of the liquids begins to increase, until at 210° C. they become completely soluble again. The solubility relations of this binary mixture are shown in Fig. 52. The closed solubility curve defines the limits of the coexistence of two layers, all points outside of the curve representing homogeneous solutions.

Complete Miscibility. The study of the vapor pressures of binary mixtures of completely miscible liquids is of great importance in connection with the possibility of separating them by the process of distillation. The experimental investigations of Konowalow * on homogeneous binary mixtures of liquids have shown that such pairs of liquids may be divided into three classes as follows: — (1) Mixtures having a maximum vapor pressure corresponding to a certain composition, e.g., propyl alcohol and water; (2) Mixtures having a minimum vapor pressure corresponding to a certain composition, e.g., formic acid and water; and (3) Mixtures having vapor pressures intermediate between the vapor pressures of the pure components, e.g., methyl alcohol and water. In considering the possibility of separating binary mixtures of liquids belonging to these three classes, it is essential to determine the composition of both solution and escaping vapor. When a pure liquid is boiled the composition of the escaping vapor is the same as that of the liquid itself, but this is, in general,

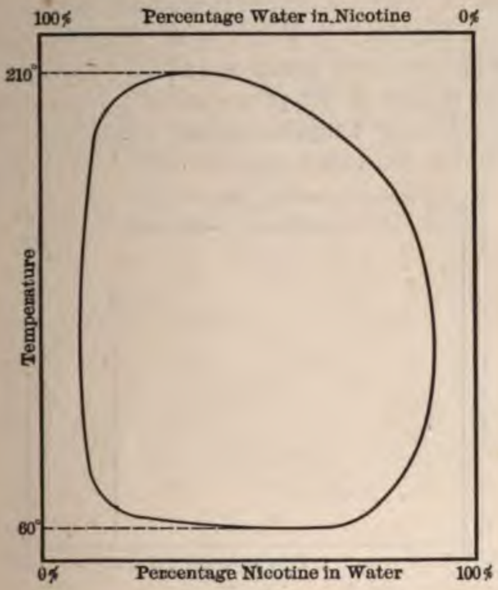


Fig. 52.

---

* Wied. Ann., 14, 34 (1881).

not the case when a binary mixture is distilled. The composition of the liquid mixture in the distilling flask generally alters continuously when such a mixture is distilled.

(1) The relation between the vapor pressure and composition of all possible mixtures of propyl alcohol and water is represented graphically in Fig. 53. In this diagram the compositions of the mixtures are plotted as abscissæ and vapor pressures as ordinates. The vapor pressures of the pure components, water and propyl alcohol, at a definite temperature are represented by *A* and *C*. The maximum in the vapor-pressure curve corresponds to a mixture containing 80 per cent of propyl alcohol. The dotted curve represents the boiling-points of the various mixtures under normal atmospheric pressure. Konowalow has shown that the vapor of a binary mixture with a minimum or maximum boiling-point has the same composition as that of the liquid. The vapor of all mixtures containing less than 80 per cent of propyl alcohol will be relatively richer in alcohol than the liquid mixture, since the vapor of propyl alcohol is quite insoluble in water. If the amount of alcohol in the mixture exceeds 80 per cent, then the vapor will be relatively richer in water. Thus, whatever may be the composition of the mixture in the distilling flask, the distillate will approximate to the composition of the mixture having the minimum boiling-point. The residue in the flask will gradually

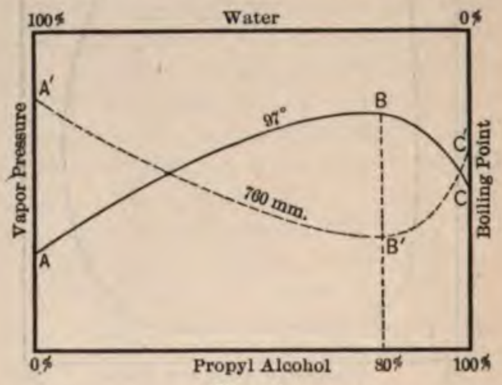


Fig. 53.

change to pure water if the original concentration were below 80 per cent, or to pure alcohol if the original concentration were above 80 per cent.

(2) The second type of binary mixture of liquids is illustrated by formic acid and water, the vapor pressure and boiling-point curves for which are shown in Fig. 54. A mixture containing 73 per cent of formic acid has a minimum vapor pressure and a maximum boiling-point. At this concentration the vapor and the liquid have the same composition. The vapor of mixtures containing less than 73 per cent of acid is relatively richer in water than the liquid, while the vapor of mixtures containing more than 73 per cent of acid contains relatively less water than the liquid. Any mixture of formic acid and water when distilled will thus leave a residue in the distilling flask containing 73 per cent of acid; this residue will distil at constant temperature like a homogeneous liquid. It was thought for a long time that such constant boiling mixtures were definite chemical compounds of the two liquids. Thus a mixture of hydrochloric acid and water containing 20.2 per cent of acid boils at 110° C. under atmospheric pressure. The composition of such a mixture corresponds very nearly to the formula, $HCl.8\,H_2O$. Roscoe * showed that these mix-

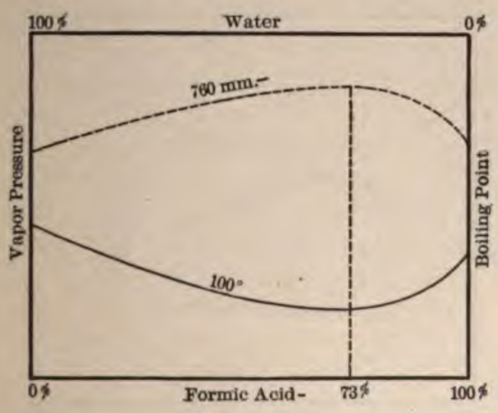


Fig. 54.

---

* Lieb. Ann. 116, 203 (1860).

tures are not definite chemical compounds since the composition of the distillate changes when the distillation is carried out under different pressures.

(3) The vapor-pressure and boiling-point curves for methyl alcohol and water, a mixture typical of the third class of completely miscible liquids, are shown in Fig. 55, the heavy line representing vapor pressures at 65°.2 C. and the dotted line the boiling points under normal atmospheric pressure. In this case the composition of both vapor and liquid alter continuously on distillation. The distillate will contain a relatively larger amount of alcohol and the residue in the distilling flask, an excess of water. If this distillate be redistilled from a clean flask, a second distillate still richer in alcohol will be obtained. By repeating this process a sufficient number of times, a more or less complete separation of the two components of the mixture can be effected. This process is termed *fractional distillation.*

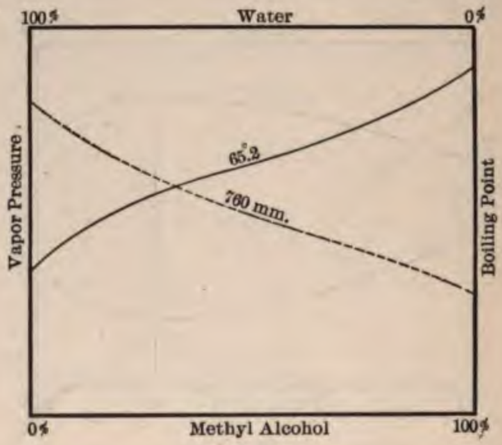


Fig. 55.

Immiscibility. When two immiscible liquids are brought together, the total vapor pressure is equal to the sum of the vapor pressures of the components; hence when such a mixture is distilled, the two liquids will pass over in the ratio of their respective vapor pressures, the boiling-point of the mixture being the temperature at which the sum of the vapor pressures of the two liquids is equal to the pressure of the atmosphere. The relation between vapor pressure and composition in this case will be represented by a horizontal line drawn at a distance above the axis of abscissæ equal to the sum of the vapor pressures of the components.

Nitrobenzene and water may be chosen as an example of a pair of liquids which are practically immiscible. Under a pressure of 760 mm. the mixture boils at 99° C. The vapor pressure of water at this temperature is 733 mm.; the vapor pressure of nitrobenzene must be 760 − 733 = 27 mm. Notwithstanding the relatively small vapor pressure of nitrobenzene in the mixture, considerable quantities of it distil over with the water. It is this fact that makes possible separations of liquids by the process of *steam distillation* so frequently employed by the organic chemist. The relative weights of water and nitrobenzene passing over in a steam distillation may be calculated as follows: — The relative volumes of steam and vapor of nitrobenzene which distil over will be in the ratio of their respective vapor pressures at the temperature of the experiment, and consequently the relative weights of the two liquids which pass over will be in the ratio, $p_1d_1 : p_2d_2$, where p_1 and p_2 denote the respective vapor pressures of water and nitrobenzene, and d_1 and d_2 the corresponding vapor densities. If w_1 and w_2 denote the weights of the two liquids in the state of vapor, then

$$w_1 : w_2 :: p_1d_1 : p_2d_2,$$

or, since vapor density is proportional to molecular weight, we may write

$$w_1 : w_2 :: p_1M_1 : p_2M_2.$$

Substituting in this proportion the values given above for the vapor pressures of steam and nitrobenzene, we have

$$w_1 : w_2 :: 733 \times 18 : 27 \times 123$$

or,

$$w_1 : w_2 :: 13{,}194 : 3321.$$

Thus the weights of water and nitrobenzene in the distillate are approximately in the ratio of 4 to 1 notwithstanding the fact that the ratio of their vapor pressures at the boiling-point of the mixture is 27 to 1. If an organic substance is not decomposed by steam, it is possible to effect an appreciable purification by steam distillation, even though its vapor pressure be relatively small. As will be seen from the above example, it is the high molecular weight of the nitrobenzene which compensates for its low vapor pressure. It is the small molecular weight of water which renders it so suitable for steam distillation.

Finally, the vapor-pressure and boiling-point relations of binary mixtures of partially miscible liquids must be considered. In general when two liquids are mixed, each lowers the vapor pressure of the other, so that the vapor pressure of the mixture is less than the sum of the vapor pressures of the components. As has already been pointed out, the composition of the two layers in a binary mixture of partially miscible liquids is independent of the relative amounts of the components present; hence the vapor pressure remains constant so long as the solution remains heterogeneous. The vapor-pressure and boiling-point curves for a binary mixture of partially miscible liquids, (isobutyl alcohol and water), are shown in Fig. 56. The horizontal portion BC, represents the vapor pressures, at 88°.5 C., of mixtures of isobutyl alcohol and water where two layers are present. The vapor

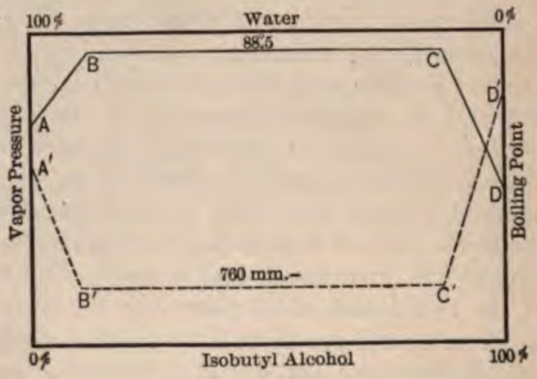


Fig. 56.

pressure of the homogeneous mixtures are represented by *AB* and *CD*, *AB* corresponding to solutions of isobutyl alcohol in water, and *CD* to solutions of water in isobutyl alcohol. The dotted line *A'B'C'D'* represents the boiling-points of all possible mixtures of isobutyl alcohol and water, under normal atmospheric pressure.

Solutions of Solids in Liquids. The solubility of a solid in a liquid is limited and is dependent upon the temperature, the nature of the solute and the nature of the solvent. When a solvent has taken up as much of a solute as it is capable of dissolving at a definite temperature, the solution is said to be *saturated*. There are two general methods for the preparation of saturated solutions: — (1) An excess of the finely-divided solute is agitated with a known amount of the solvent, at a definite temperature, until equilibrium is attained; (2) the solvent is heated with an excess of the solute to a temperature higher than that at which saturation is required, and then cooled in contact with the solid solute to the desired temperature. Both of these methods give equally satisfactory results provided sufficient time is allowed for the establishment of equilibrium, and provided the solid substance is always present in excess. The solubility of a solid in a liquid may be expressed as the number of grams of the solute in a given mass or volume of solvent or solution, but it is usually expressed as the number of grams of solute in 100 grams of solution. The solubility of solids has recently been shown to be somewhat dependent upon their state of division. Thus, Hulett[*] has found that a saturated solution of gypsum at 25° C. contains 2.080 grams of $CaSO_4$ per liter, whereas when very finely divided gypsum is shaken with this solution, it is possible to increase the content of dissolved $CaSO_4$ to 2.542 grams per liter. When a saturated solution is cooled, every trace of solid solute being excluded, the excess of dissolved solid may not separate. Such a solution is said to be *supersaturated*.

As a general rule the solubility of solids in liquids increases with the temperature, as shown in Fig. 57. Several exceptions to this rule are known, among which may be mentioned calcium hydroxide, calcium sulphate above 40° C., and sodium sulphate between the temperatures of 33° C. and 100° C.

---

[*] Jour. Am. Chem. Soc., **27**, 49 (1905).

Solubility curves are usually continuous, but exceptions to this rule are common: the solubility curve of sodium sulphate furnishes an illustration. The discontinuity in the solubility curve of sodium sulphate is due to the fact that we are not dealing with one solubility curve, but with two solubility curves. At temperatures below 33° C., the dissolved salt is in equilibrium with the decahydrate, $Na_2SO_4.10\,H_2O$, whereas at temperatures above 33° C. the dissolved salt is in equilibrium with the anhydrous salt, Na_2SO_4. The solubility of $Na_2SO_4.10\,H_2O$ increases with the temperature, while the solubility of Na_2SO_4 diminishes. That we are actually dealing with two solubility curves, is proved by the fact that the solubility curves of the hydrated and anhydrous salts in supersaturated solutions are continuations of the corresponding curves for saturated solutions, as shown by the dotted

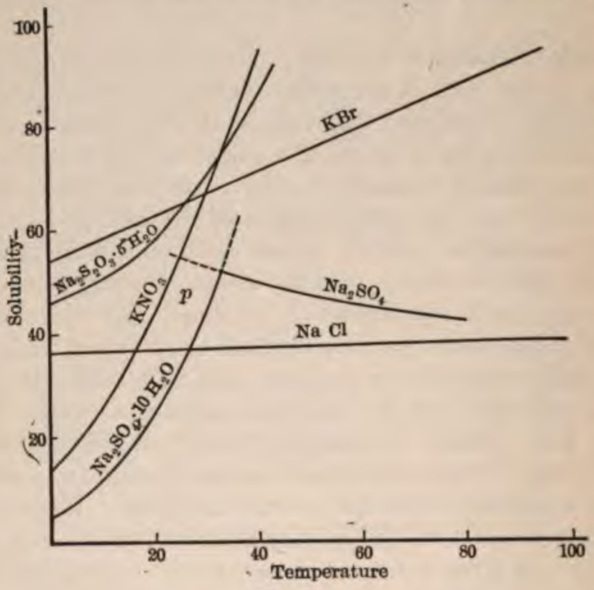


Fig. 57.

curves in Fig. 57. If we select any point, such as *p*, lying between a dotted curve and a full curve, it is apparent that it represents a solution supersaturated with respect to $Na_2SO_4.10\,H_2O$, but unsaturated with respect to Na_2SO_4. If pure anhydrous sodium sulphate be shaken with this solution it will slowly dissolve, whereas if a trace of the hydrated salt be added, the solution will deposit $Na_2SO_4.10\,H_2O$, until the amount remaining in solution corresponds to the solubility of the hydrate at that temperature. Supersaturated solutions of some substances can be preserved indefinitely, provided all traces of the solid phase are excluded. Such solutions are called *metastable*. On the other hand there are some supersaturated solutions which deposit the excess of solid solute even when all traces of it are excluded. These solutions are termed *labile*. The distinction between metastable and labile solutions is not sharp. If a metastable solution is sufficiently cooled, or if its concentration is sufficiently increased, it may be made to pass over into the labile condition. The concentration at which this transition occurs is termed the *metastable limit*. The stability of supersaturated solutions has recently been shown by Young * to be greatly influenced by vibrations or sudden shocks within the solution. He has been able to control the amount of overcooling in a supersaturated solution, by altering the intensity of the vibrations due to the friction between glass or metal surfaces within the solution.

Very little is known concerning the relation between solubility and the specific properties of solute and solvent.

Owing to the fact that the change in volume resulting from the solution of a solid in a liquid is very small, the effect of pressure on the solution is almost negligible. The chief factors conditioning the change in solubility due to increasing pressure, are the heat of solution of the solute in the nearly saturated solution, and the change in volume on solidification. Very few experiments have been made to determine the effect of pressure on solubility. Van't Hoff states that the solubility of a solution of ammonium chloride, a salt which expands when dissolved, decreases by 1 per cent for 160 atmospheres, while the solubility of copper sulphate, a salt which contracts when dissolved, increases by 3.2 per cent for 60 atmospheres.

---

* Jour. Am. Chem. Soc., 33, 148 (1911).

Solid Solutions. In general, when a dilute solution is sufficiently cooled the solvent separates in the form of crystals which are almost entirely free from the solute. When, however, the temperature of a solution of iodine in benzene is reduced to the freezing-point, the crystals which separate are found to contain iodine. Furthermore, the depression of the freezing-point of the solvent is found to be less than that calculated on the assumption that the solvent crystallizes uncontaminated with the solute. Such solutions were first studied by van't Hoff.* He found that when the concentration of such abnormal solutions is varied, the ratio of the amount of solute in the liquid solvent to the amount of solute in the solidified solvent remains constant. Thus, in solutions of iodine in benzene, the ratio of the concentration of iodine in the liquid to its concentration in the crystallized benzene is constant. In the following table c_1 is the concentration of iodine in the liquid benzene, and c_2 is the concentration of iodine in the solid benzene.

c_1	c_2	c_1/c_2
3.39	1.279	0.377
2.587	0.925	0.358
0.945	0.317	0.336

Van't Hoff pointed out the analogy between the distribution of the solute between the solid and liquid solvent, and the distribution of a gas between a liquid and the free space above it. In other words, the distribution follows Henry's law for the solution of a gas in a liquid. Since the crystals containing both solute and solvent are perfectly homogeneous, van't Hoff suggested that they be regarded as *solid solutions*. The mixed crystals which separate from solutions of isomorphous substances being chemically and physically homogeneous, are to be considered as solid solutions. Many alloys possess the properties characteristic of solid solutions; hardened steel, for example, being regarded as a homogeneous solid solution of carbon in iron. One of the characteristic properties of a dissolved substance is its tendency to diffuse into the pure solvent. Interesting experiments performed by Roberts-Austen * have shown that even solids have the property of mixing by diffusion. Thus, by keeping gold and lead in contact at constant temperature for four years, he was able to detect the presence of gold in the layer of lead at a distance of 7 mm. from the surface of separation. Many other instances of diffusion in solids have been observed.†

---

* Zeit. phys. Chem., 5, 322 (1890).

Instances of gases and liquids dissolving in solids are also known. Thus platinum, palladium, charcoal and other substances have the property of taking up large volumes of hydrogen. This phenomenon, known as *occlusion*, is but little understood. Van't Hoff has suggested that when hydrogen dissolves in palladium we are really dealing with two solid solutions: one a solution of hydrogen in palladium and the other a solution of palladium in solid hydrogen, the system being analogous to that of two partially miscible liquids.

Certain natural silicates, the so-called zeolites, are transparent and homogeneous. Since they contain varying quantities of water they may be regarded as examples of solutions of liquids in solids. This classification is further justified by the fact that portions of the water may be removed and replaced by other substances, such as alcohol, with apparently no change in the transparency or homogeneity of the mineral.

PROBLEMS.

1. 2.3 liters of hydrogen under a pressure of 78 cm. of mercury, and 5.4 liters of nitrogen at a pressure of 46 cm. were introduced into a vessel containing 3.8 liters of carbon dioxide under a pressure of 27 cm. What was the pressure of the mixture? *Ans.* 140 cm. of mercury.

2. Air is composed of 20.9 volumes of oxygen and 79.1 volumes of nitrogen. At 15° C. water absorbs 0.0299 volumes of oxygen and 0.0148

---

* Proc. Roy. Soc., **67**, 101 (1900).

† See Report on Diffusion in Solids, by C. H. Desch, Chem. News, **106**, 153 (1912).

volumes of nitrogen, the pressure of each being that of the atmosphere. Calculate the composition of the mixture of gases absorbed by the water.
Ans. 34.8% by vol. of O, and 65.2% by vol. of N.

3. The vapor pressure of the immiscible liquid system, aniline-water, is 760 mm. at 98° C. The vapor pressure of water at that temperature is 707 mm. What fraction of the total weight of the distillate is aniline.
Ans. 0.28.

4. The boiling-point of the immiscible liquid system, naphthalene-water, is 98° C. under a pressure of 733 mm. The vapor pressure of water at 98° C. is 707 mm. Calculate the proportion of naphthalene in the distillate.
Ans. 0.207.

CHAPTER X.

DILUTE SOLUTIONS AND OSMOTIC PRESSURE.

Osmotic Pressure. In the preceding chapter reference was made to the fact that diffusion is a characteristic property of solutions. If a few cubic centimeters of a concentrated solution of cane sugar are placed at the bottom of a tall cylinder, and water is added, care being taken to prevent mixture, the sugar immediately begins to diffuse into the water, the process continuing until the concentration of sugar is the same throughout the liquid. The sugar molecules move from a region of high concentration to a region of low concentration, the rate of diffusion being relatively slow owing to the viscosity of the medium. A similar process is encountered in the study of gases, but the rate of gaseous diffusion is extremely rapid. In terms of the kinetic theory, the movement of the molecules of a gas from regions of high concentration to regions of low concentration, is to be considered as due to the pressure of the gas. By analogy, we may regard the process of diffusion in solutions as a manifestation of a driving force, known as the *osmotic pressure.*

Semi-permeable Membranes. The use of a semi-permeable membrane for the measurement of the partial pressure of nitrogen in a mixture of nitrogen and hydrogen, has already been explained. A similar method may be employed for the measurement of the osmotic pressure of a solution, provided a suitable semi-permeable membrane can be found. Such a membrane must prevent the passage of the molecules of solute and must be readily permeable to the molecules of solvent; it must exert a selective action on solute and solvent. If a solution is separated from the pure solvent by a semi-permeable membrane, diffusion of the solute is no longer possible. Since equilibrium of the system can only be attained when the concentrations on both sides of the membrane are equal, it follows that the solvent must pass through the membrane and dilute the more concentrated solution. A number of semi-permeable membranes have been discovered which are readily permeable to water and nearly, if not entirely, impermeable to various solutes. About the middle of the eighteenth century Abbé Nollet discovered that certain animal membranes are permeable to water but not to alcohol.

Artificial semi-permeable membranes were first prepared by M. Traube.* If a glass tube, provided with a rubber tube and pinch-cock, be partially filled, by suction, with a solution of copper sulphate, and then immersed in a solution of potassium ferrocyanide, a thin film of copper ferrocyanide will be formed at the junction of the two solutions. When the film has once been formed, further precipitation of copper ferrocyanide will cease, the solutions on either side of the film remaining clear. Traube showed that this membrane is semi-permeable. He also showed that a number of other gelatinous precipitates possess the property of semi-permeability. A membrane formed in the above manner is easily ruptured and is wholly inadequate for quantitative or even qualitative experiments. Pfeffer † devised a method for strengthening the membrane. By depositing the precipitate in the walls of a porous clay cup, the area of unsupported membrane is greatly diminished and its resisting power correspondingly increased. Pfeffer directs that the cup to be used for this purpose must be throughly washed, and its walls allowed to become completely permeated with water. The cup is then filled to the top with a solution of copper sulphate, containing 2.5 grams per liter, and allowed to stand for several hours in a solution of potassium ferrocyanide, containing 2.1 grams per liter. The two solutions diffuse through the walls of the cup and on meeting, deposit a thin membrane of copper ferrocyanide. When precipitation is complete, the cup is thoroughly washed and soaked in water. The cup is then filled to the top with a solution of cane sugar, and a rubber stopper, fitted with a long glass tube of narrow bore, is inserted, care being taken to exclude air-bubbles. The stopper is then made fast with a suitable cement, and the cup completely immersed in a beaker of water. The completed apparatus is shown in Fig. 58. If the formation of the membrane has been successful, the level of the liquid in the vertical glass tube will slowly rise and will eventually attain a height of several meters. If the membrane is sufficiently strong and no leaks develop, the passage of water through the membrane will continue until the hydrostatic pressure of the column of liquid in the tube is great enough to overcome the tendency of the water to force its way into the sugar solution. As a general rule, the membrane becomes ruptured before equilibrium is attained.

---

* Archiv. für Anat. und Physiol., p. 87 (1867).

† Osmotische Untersuchungen, Leipzig, 1877.

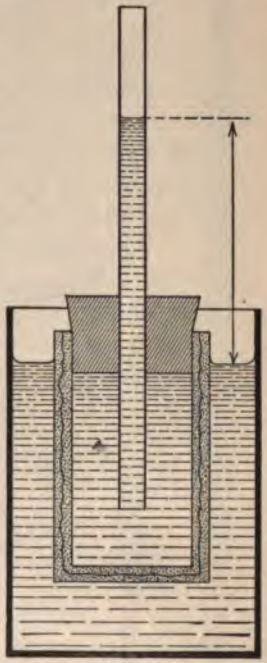


Fig. 58.

Measurement of Osmotic Pressure. The first direct measurements of osmotic pressure were made by Pfeffer. His experiments deserve brief consideration, since the results obtained furnish the basis of the modern theory of solution. The cell used was similar to that described above, but instead of employing a vertical glass tube as a manometer, the cup was connected, as shown in Fig. 59, with a closed mercury manometer. The substitution of the closed for the open manometer is necessitated by the fact, that with an open manometer so much water entered the cell that the concentration of the solution became appreciably diminished, and the pressure actually measured corresponded to a solution of smaller concentration than that introduced into the cell. With the closed manometer, when a trace of water has entered the cell, sufficient pressure is developed to prevent the further entrance of more water. Pfeffer calculated that with a cell, the capacity of which was 16 cc., the volume of water entering before equilibrium was attained, did not exceed 0.14 cc. In his experiments, Pfeffer determined the density of the cell contents before and after measurement of the osmotic pressure, and corrected for any change in concentration. With this apparatus he made numerous measurements of the osmotic pressures of different solutions, the entire apparatus being immersed in a constant-temperature bath. With solutions of cane sugar he obtained the results given in the accompanying table, where *C* denotes the percentage concentration of the solution, and *P* the corresponding osmotic pressure, expressed in centimeters of mercury. The temperature varied from 13.5° C. to 14°.7 C.

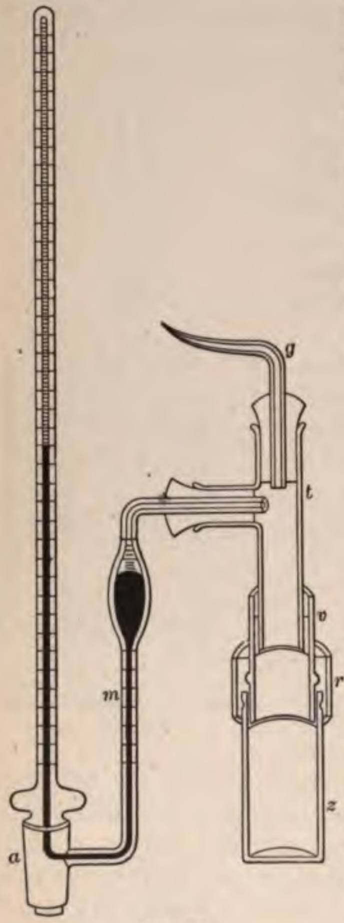


Fig. 59.

C	*P*	*P/C*
1	53.5	53.5
2	101.6	50.8
4	208.2	52.0
6	307.5	51.2

It is evident from these results, that the osmotic pressure is proportional to the concentration of the solution, since *P/C* is approximately constant. The deviations from constancy in the ratio of pressure to concentration may be ascribed to experimental errors, since the difficulties involved in these measurements are very great. Pfeffer also studied the influence of temperature on osmotic pressure, and showed that as the temperature is raised the pressure increases. The following table gives his results for a 1 per cent solution of cane sugar.

Temperature.	Osmotic Pressure.
	cm.
6°.8	50.5
13°.2	52.1
14°.2	53.1
22°.0	54.8
36°.0	56.7

Osmotic Pressure and the Nature of the Membrane. Pfeffer also studied the effect of the nature of the membrane on osmotic pressure. In addition to copper ferrocyanide, he used membranes of calcium phosphate and Prussian blue. His results seemed to indicate that the magnitude of the osmotic pressure developed, was dependent upon the nature of the membrane used.

The variations observed have since been shown to have been due to leakage of the calcium phosphate and Prussian blue membranes, the copper ferrocyanide membrane being the only one which was capable of withstanding the pressure. Ostwald * has devised an ingenious theoretical demonstration of the fact that osmotic pressure must be independent of the nature of the membrane employed in measuring it. Let *A* and *B*, in Fig. 60, represent two different semi-permeable membranes placed in a glass tube of wide bore. Let us imagine the space between the two membranes to be filled with a solution, and the tube immersed in a vessel of water. If the osmotic pressures developed at *A* and *B* are p_1 and p_2 respectively, and p_2 is less than p_1, then water will pass through *A* until the pressure p_1 is reached. Since the pressure at *B* only reaches the value p_2, however, the pressure p_1 can never be attained, and a steady stream of water from *A* to *B*, under the pressure $p_1 - p_2$, will result. This, however, would be a perpetual motion, and since this is impossible, the osmotic pressures at the two membranes must be the same.

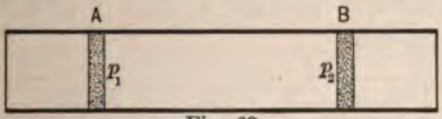


Fig. 60.

---

* Lehrb. d. allg. Chem., I., p. 662.

Theoretical Value of Osmotic Pressure. The physico-chemical significance of Pfeffer's results was first perceived by van't Hoff.* In a remarkably brilliant paper, he pointed out the existence of a striking parallelism between the properties of gases and the properties of dissolved substances.

We have already called attention to the analogy between osmotic pressure and gas pressure: we now proceed to trace the connection between osmotic pressure, volume and temperature, as first pointed out by van't Hoff. Pfeffer's experiments showed that at constant temperature, the ratio, P/C, is constant for any one solute. Since the concentration varies inversely as the volume in which a definite amount of solute is dissolved, we obtain, by substituting $1/V$ for C, the equation, $PV =$ constant, which is plainly the analogue of the familiar equation of Boyle for gases. An examination of Pfeffer's data for osmotic pressures at different temperatures, convinced van't Hoff that the law of Gay-Lussac is also applicable to solutions.

In the following table, the osmotic pressures in atmospheres for a 1 per cent solution of cane sugar at different temperatures are recorded, together with the pressures calculated on the assumption that the osmotic pressure is directly proportional to the absolute temperature.

Temperature.	P (obs.).	P (calc.).
6°.8	0.664	0.665
13°.7	0.691	0.681
15°.5	0.684	0.686
22°.0	0.721	0.701
32°.0	0.716	0.725
36°.0	0.746	0.735

Since the laws of Boyle and Gay-Lussac are both applicable, we may write an equation for dilute solutions corresponding to that already derived for gases, or

$$PV = R'T,$$

in which P is the osmotic pressure of a solution containing a definite weight of solute in the volume, V, of solution, T being the absolute temperature of the solution and R' a constant corresponding to the molecular gas constant.

---

* Zeit. phys. Chem., 1, 481 (1887).

The molecular gas constant R has already been evaluated and has been found to be equal to 0.0821 liter-atmosphere.

Making use of Pfeffer's data, van't Hoff calculated the value of R' in the above equation, in the following manner: the osmotic pressure of a 1 per cent solution of cane sugar at 0° C. is 0.649 atmosphere, and since the concentration of the solution is 1 per cent, the volume of solution containing 1 mol of sugar, will be 34,200 cc. or 34.2 liters. Substituting these values in the equation, we have

$$R' = \frac{PV}{T} = \frac{0.649 \times 34.2}{273} = 0.0813 \text{ liter-atmos.},$$

a value which is nearly the same as that of the molecular gas constant, R. The equality of R and R' leads to a conclusion of the greatest importance, as was pointed out by van't Hoff, viz., "*the osmotic pressure exerted by any substance in solution is the same as it would exert if present as a gas in the same volume as that occupied by the solution, provided that the solution is so dilute that the volume occupied by the solute is negligible in comparison with that occupied by the solvent.*" It should be remembered that we are not justified in concluding from this proposition of van't Hoff, that osmotic pressure and gaseous pressure have a common origin. While the origin of osmotic pressure may be kinetic, it is also conceivable that it may result from the mutual attraction of solvent and solute, or that it may bear some relation to the surface tension of the solution. Up to the present time no wholly satisfactory explanation of the cause of osmotic pressure has been advanced.

Just as 1 mol of gas at 0° C. and 760 mm. pressure occupies a volume of 22.4 liters, so when 1 mol of a substance is dissolved and the solution diluted to 22.4 liters at 0° C., it will exert an osmotic pressure of 1 atmosphere. In other words, *molar weights, or quantities proportional to molar weights, of different substances, when dissolved in equal volumes of the same solvent exert the same* *osmotic pressure.* If we deal with n mols of solute instead of 1 mol, the general equation becomes

$$PV = nRT.$$

But $n = g/M$, where g is the number of grams of solute per liter, and M is its molecular weight. Substituting in the preceding equation, we have

$$PV = g/M \cdot RT,$$

or,

$$M = \frac{gRT}{PV}.$$

Since P, V, g, R and T are all known, M can be calculated. The direct measurement of the osmotic pressure of a solution does not afford a practical method for the determination of the molecular weight of dissolved substances, because of the experimental difficulties involved and the time required for the establishment of equilibrium. There are other and simpler methods for determining molecular weights in solution, based upon certain properties of solutions which are proportional to their respective osmotic pressures.

Recent Work on the Direct Measurement of Osmotic Pressure. It is only within the past decade that the investigations of Pfeffer have been confirmed and extended by elaborate and systematic experiments on the direct measurement of osmotic pressure. Morse and his co-workers,* while employing a method essentially the same as that of Pfeffer, have, as the result of much patient labor, brought the apparatus to such a high state of perfection, that the experimental errors are now estimated to affect only the second place of decimals in the numerical data expressing osmotic pressures in atmospheres. The most important of the improvements introduced by Morse are the following: — (1) the improvement of the quality of the membrane; (2) the improvement of the connection between the cell and the manometer, and (3) the improvement of the means of accurately measuring the pressure. The membrane of copper ferrocyanide is deposited electrolytically. After thorough washing and soaking in water, the porous cup, made from specially prepared clay, is filled with a solution of potassium ferrocyanide and immersed in a solution of copper sulphate. An electric current is then passed from a copper electrode in the solution of copper sulphate, to a platinum electrode immersed in the solution of potassium ferrocyanide. This drives the copper and ferrocyanide ions toward each other, and the membrane of copper ferrocyanide is thus formed in the walls of the cup. The passage of the current is continued until the electrical resistance reaches a value of about 100,000 ohms. The cell is then rinsed, and soaked in water for several hours, and then the electrolytic treatment is repeated until the electrical resistance attains a maximum value. A solution of cane sugar is now introduced into the cell, which is connected with the manometer and immersed in water. When the pressure has attained its maximum value, the apparatus is dismantled and the cell, after thorough washing and soaking in water, is again subjected to the electrolytic process of membrane forming. In this way the weak places in the membrane which may have yielded to the high pressure, can be repaired, and by continued repetition of this treatment the membrane can ultimately be brought to its maximum power

---

* Am. Chem. Jour., **26**, 80 (1901); **34**, 1 (1905); **36**, 1, 39 (1906); **37**, 324, 425, 558 (1907); **38**, 175 (1907); **39**, 667 (1908); **40**, 1, 194 (1908); **41**, 1, 257 (1909).

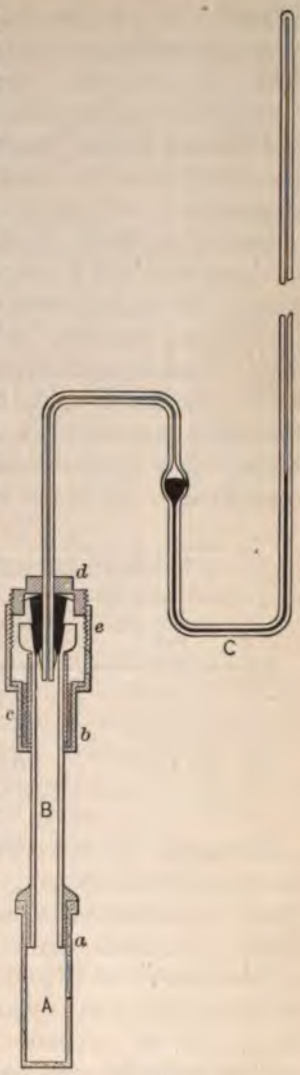


Fig. 61.

of resistance. A sketch of the Morse apparatus is shown in Fig. 61. A description of the details of this apparatus lies beyond the scope of this book. The results of the work of Morse and his students are of the highest importance. The osmotic pressures of solutions of cane sugar and dextrose have been shown to be proportional to the respective concentrations, provided the concentration is referred to unit volume of solvent instead of unit volume of solution. Thus in their experiments, the solutions were made up containing from 0.1 to 1.0 mol of solute in 1000 grams of water. Morse calls such solutions *weight-normal solutions* in contrast to *volume-normal solutions,* in which 1 mol or a fraction of a mol of solute is dissolved in water and the solution diluted to 1 liter. The following data taken from the work of Morse, shows that when concentration is expressed on the weight-normal basis, there is direct proportionality between osmotic pressure and concentration. The figures refer to solutions of dextrose at 10° C.

Molar Concentration.		Osmotic Pressure.	
Per 1000 gm. Water.	Per Liter of Solution.	In Atmos.	Relative to First as Unity.
0.1	0.099	2.39	1.00
0.2	0.196	4.76	1.99
0.5	0.474	11.91	4.98
1.0	0.901	23.80	9.96

Morse and his co-workers also conclude from their experiments at temperatures ranging from 0° C. to 25° C., that the temperature coefficients of osmotic pressure and gas pressure are practically identical. In other words, their results confirm the conclusions of van't Hoff, that the law of Gay-Lussac is applicable to solutions. The results of the experiments of Morse are of special interest in connection with the proposition of van't Hoff, that the osmotic pressure of a dilute solution is the same as that which the solute would exert if it were gasified at the same temperature and occupied the same volume as the solution. The data in the following table is taken from the work of Morse on solutions of cane sugar at 15° C. In addition to the observed osmotic pressures, the table contains the corresponding gas pressures, calculated (1) on the assumption that the solute when gasified occupies the same volume as the solution (proposition of Van't Hoff), and (2) on the assumption that it occupies the same volume as the solvent alone.

Molar Concentration.		Osmotic Pressure in Atmos.		
Per 1000 gm. of Water.	Per Liter of Solution.	Obs.	Calc. (a).	Calc. (b).
0.1	0.098	2.48	2.30	2.35
0.2	0.192	4.91	4.51	4.70
0.4	0.369	9.78	8.67	9.40
0.6	0.533	14.86	12.51	14.08
0.8	0.684	20.07	16.07	18.79
1.0	0.825	25.40	19.38	23.49

The calculated pressures, recorded in the last column, are in much closer agreement with the observed osmotic pressures, than are the calculated pressures, recorded in the fourth column of the table. The proposition of van't Hoff should then be modified to read as follows: — *A dissolved substance in dilute solution exerts an osmotic pressure equal to that which it would exert if it were gasified at the same temperature, and the volume of the gas were reduced to that of the solvent in the pure state.* The investigations of Morse and his co-workers may be summarized thus: — (1) the law of Boyle is applicable to dilute solutions, provided the concentration is referred to 1000 grams of solvent and not to 1 liter of solution; (2) the law of Gay-Lussac is also applicable to dilute solutions, that is, the temperature coefficients of osmotic pressure and gas pressure are equal, and (3) the small departures from the theoretical values of the osmotic pressures may be traced to hydration of the solute.

Direct measurements of the osmotic pressure of concentrated solutions of cane sugar, dextrose and mannite have been made by the Earl of Berkeley and E. G. J. Hartley.* The method employed by these investigators is slightly different from that of Pfeffer or Morse; the tendency of water to pass through the semi-permeable membrane is offset by the application of a counter pressure to the solution. A membrane of copper ferrocyanide is deposited electrolytically very near the outer surface of a tube of porous porcelain. This tube is placed co-axially within a large cylindrical vessel of gun metal, an absolutely tight joint between the two being secured by an ingenious system of dermatine rings and clamps. The open ends of the porcelain tube are closed by rubber stoppers fitted with capillary tubes bent at right angles, one of the latter being provided with a glass stop-cock. When a determination of osmotic pressure is to be made, the apparatus is placed in a horizontal position and water is introduced into the porcelain tube, completely filling it and the connecting capillary tubes up to a certain level. The gun metal vessel is then filled with the solution, and connected with an auxiliary apparatus by means of which a gradually increasing hydrostatic pressure can be applied. If no pressure is applied to the solution, water will pass through the semi-permeable membrane into the solution, and the level of the water in the capillary tubes will fall. In carrying out a measurement, therefore, as soon as the solution is introduced into the gun metal vessel, hydrostatic pressure is applied, the magnitude of the pressure being so adjusted as to counterbalance the osmotic pressure of the solution. The level of the water in the capillary tubes serves to indicate the relative magnitudes of the osmotic and hydrostatic pressures. When the level of the water in the capillary tubes remains constant, the two pressures are in equilibrium. The following are the values of the equilibrium pressures of solutions of cane sugar, dextrose and mannite at 0° C. It must be remembered that when the two pressures are in equilibrium, there is always a pressure of one atmosphere on the solvent.

---

* Proc. Roy. Soc., **73**, 436 (1904); Trans. Roy. Soc. A., **206**, 481 (1906).

As will be seen the pressures developed in the more concentrated solutions are enormous and it is a surprising fact, that even in cases where the highest pressures were measured, hardly a trace of sugar was found in the pure solvent, the membrane retaining its property of semi-permeability throughout the entire range of pressures. The figures in the third column are calculated

CANE SUGAR.

Conc. gm. per Liter.	Osmotic Pressure in Atmospheres.	
	Obs.	Calc.
180.1	13.95	13.95
300.2	26.77	28.74
420.3	43.97	32.55
540.4	67.51	41.85
660.5	100.78	51.16
750.6	133.74	58.14

DEXTROSE.

Conc. gm. per Liter.	Osmotic Pressure in Atmospheres.	
	Obs.	Calc.
99.8	13.21	13.21
199.5	29.17	26.41
319.2	53.19	42.25
448.6	87.87	59.28
548.6	121.18	72.61

MANNITE.

Conc. gm. per Liter.	Osmotic Pressure in Atmospheres.	
	Obs.	Calc.
100	13.1	13.1
110	14.6	14.4
125	16.7	16.4

n the assumption that there is direct proportionality between smotic pressure and concentration. It is apparent that in every ase the observed osmotic pressure is greater than the calculated. ven when the concentrations are expressed on the weight-normal basis, as recommended by Morse, the osmotic pressure increases more rapidly than the concentration.

This is well shown in the accompanying diagram, Fig. 62, due to the Earl of Berkeley. In this diagram, the osmotic pressures of solutions of cane sugar are plotted against concentrations, curve *A* representing the actually observed osmotic pressures; curve *C* being traced on the assumption that osmotic pressure may be calculated from the equation, $PV = RT$, where V denotes the volume of solvent containing 1 mol of cane sugar; and curve *B*, a straight line, being drawn on the assumption that osmotic pressure may be calculated from the equation, $PV = RT$, where V represents the volume of solution containing 1 mol.

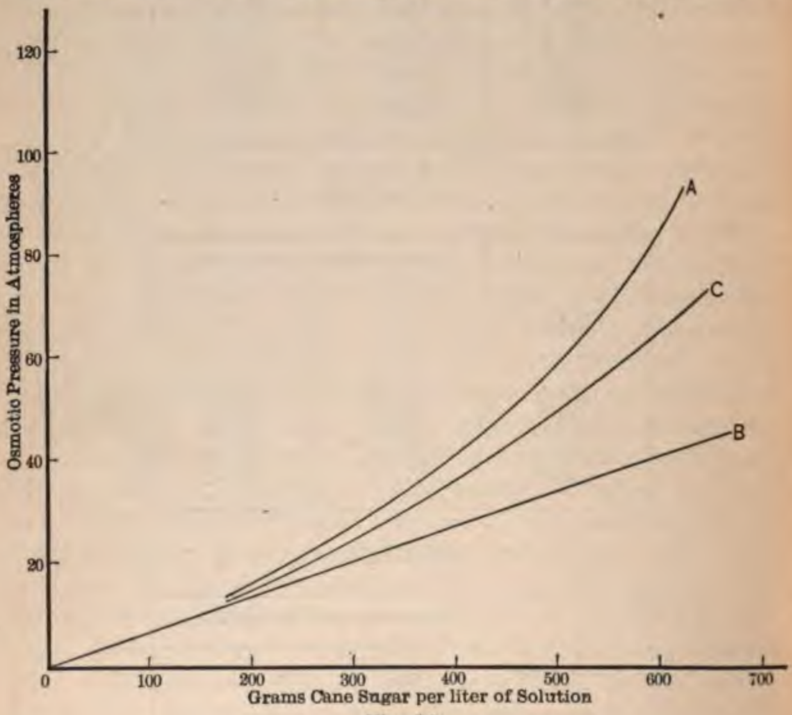


Fig. 62.

While the theoretical and observed values of the osmotic pressure are approximately equal in the more dilute solutions, it is obvious that the observed values of the osmotic pressure of the concentrated solutions are always greater than the calculated values, even when the calculation is made on the assumption that V in the equation, $PV = RT$, is the volume of the solvent. The abnormally high osmotic pressures observed by the Earl of Berkeley have been discussed by Callendar * who suggests hydration of the solute as a probable cause.

He shows, that if 5 molecules of water are assumed to be associated with each molecule of cane sugar in the most concentrated solutions studied by the Earl of Berkeley, the discrepancy between the observed and calculated values of the osmotic pressure disappears.

Comparison of Osmotic Pressures. Although the difficulties involved in the direct determination of osmotic pressure are many, these can be avoided by the employment of one of several indirect methods which have been devised for the comparison of osmotic pressures. All of these methods depend upon the exchange of water which occurs when two solutions are separated by a semi-permeable membrane. The movement of the water will always be in such a direction as to tend to equalize the osmotic pressures on opposite sides of the membrane, or, in other words, the transfer of water will take place from the solution with the lesser osmotic pressure to the solution with the greater osmotic pressure.

The Plasmolytic Method. In this method, solutions of various substances are prepared, the concentration of each being such that its osmotic pressure is the same as that of a particular plant cell. Obviously the osmotic pressures of all of these solutions must be equal: such solutions are said to be *isotonic* or *isosmotic*. The plasmolytic method for the comparison of osmotic pressures was developed by the Dutch botanist, De Vries.† This method depends upon the shrinking or swelling of the protoplasmic sac of plant cells when they are immersed in a solution whose osmotic pressure differs from that of their own sap. De Vries found that the cells of *Tradescantia discolor*, *Curcuma rubricaulis*, and *Begonia manicata* fulfil the necessary conditions, viz.; the cell walls are strong and resist alteration when immersed in solutions, the cells are readily permeable to water, and the cell contents are colored, thus enabling the slightest contraction or expansion to be detected. The cell walls are lined on the inside with a thin, elastic, semi-permeable membrane which encloses the colored contents of the cell. The content of the cell consists of an aqueous solution of several substances, among which may be mentioned glucose, potassium and calcium malate, together with coloring matter. The osmotic pressure of the cell contents ranges from four to six atmospheres. The semi-permeable membrane expands when the contents of the cell increases and contracts when the contents diminishes. In making a comparison of osmotic pressures by this method, tangential sections are cut from the under side of the mid-rib of the leaf of one of the above plants, e.g., *Tradescantia discolor*, and are placed in the solution whose osmotic pressure it is desired to compare with that of the cell contents. The cells are then observed under the microscope, any decrease in pressure below the normal resulting in a detachment of the semi-permeable membrane from one or more points of the cell wall. This contraction always occurs when the cells are immersed in a concentrated solution, the phenomenon being termed *plasmolysis*. When the solution in which the cells are placed has a lower osmotic pressure than the cell contents, no visible effect is produced, the increased pressure within the cell simply forcing the membrane closer to the rigid cell walls. By starting with a concentrated solution, the osmotic pressure of which is greater than that of the cell, and gradually diluting it, a concentration will ultimately be reached at which the elastic membrane will just completely fill the cell. This solution is isotonic with the cell contents. In this method the very reasonable assumption is made that all of the cells have the same osmotic pressure, any differences which might have existed having equalized themselves in the living plant. The microscopic appearance of cells of *Tradescantia discolor* when immersed in different solutions is shown in Fig. 63. The appearance of the normal cell when immersed in water or in a solution whose osmotic pressure is less than that of the cell contents, is shown in *A*. When the cell is immersed in a 0.22 molar solution of cane sugar it appears as in *B*, this solution having a greater osmotic pressure than the cell contents. When the cell is immersed in a molar solution of potassium nitrate, there is marked plasmolysis, as shown in *C*. De Vries determined the concentrations of a large number of solutions which were isotonic with the cell contents. He expressed his results in terms of the *isotonic coefficient*, which he defined as the reciprocal of the molar concentration. The isotonic coefficient of potassium nitrate was taken equal to 3. A few of De Vries' results are given in the following table.

---

* Proc. Roy. Soc. A., **80**, 466 (1908).

† Jahrb. wiss. Botanik., **14**, 427 (1884); Zeit. phys. Chem., **2**, 415 (1888); **3**, 103 (1889).

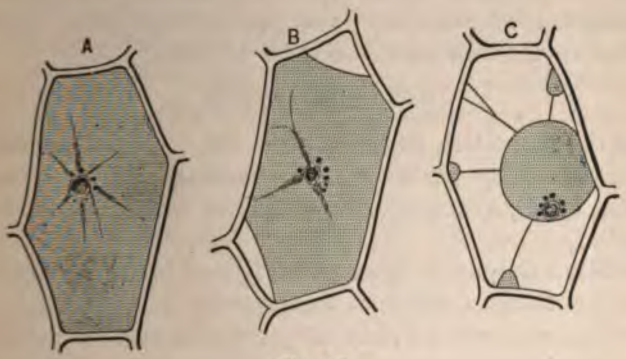


Fig. 63.

Substance.	Formula.	Isotonic Coefficient.
Glycerol	$C_3H_8O_3$	1.78
Glucose	$C_6H_{12}O_6$	1.81
Cane sugar	$C_{12}H_{22}O_{11}$	1.88
Malic acid	$C_4H_6O_5$	1.98
Tartaric acid	$C_4H_6O_6$	2.02
Citric acid	$C_6H_8O_7$	2.02
Potassium nitrate	KNO_3	3.00
Magnesium chloride	$MgCl_2$	4.33

De Vries applied the plasmolytic method to the determination of the molecular weight of raffinose. At that time there was considerable uncertainty as to the correct formula of crystallized raffinose, three different formulas, all consistent with the results of analysis, having been proposed as follows: — $C_{18}H_{32}O_{16}.5\,H_2O$, $C_{12}H_{22}O_{11}.3\,H_2O$, and $C_{36}H_{64}O_{32}$. De Vries found that a 3.42 per cent solution of cane sugar was isotonic with a 5.96 per cent solution of raffinose. Letting the unknown molecular weight of raffinose be represented by M, then

$$3.42 : 5.96 :: 342 : M.$$

Solving the proportion we have, $M = 596$. This result has since been confirmed by purely chemical methods, and the formula, $C_{18}H_{32}O_{16}.5\,H_2O$, the molecular weight of which is 594, is thus established.

The Blood Corpuscle Method. The red blood corpuscle is a cell, the contents of which is enclosed by a thin elastic semipermeable membrane. Unlike the plant cells, there is no resistant cell wall to give support to the membrane, so that when red blood corpuscles are immersed in water they at first swell, owing to the osmotic pressure developed, and finally burst. When the membrane is ruptured, the coloring matter of the cell, the hæmoglobin, escapes and the water acquires a deep red color.

Advantage of this behavior of red blood corpuscles was taken by Hamburger * for the comparison of osmotic pressures. He found that when a 1.04 per cent solution of potassium nitrate is added to the defibrinated blood of a bullock, the corpuscles will settle completely to the bottom, while the supernatant liquid will remain clear. On the other hand, if a 0.96 per cent solution of potassium nitrate is used, the corpuscles will not settle and the supernatant liquid becomes colored. If more dilute solutions of potassium nitrate are used, the solution acquires a still deeper color. By careful adjustment, a concentration of potassium nitrate can be found in which the red blood corpuscles will just settle. In like manner, the concentration of solutions of other substances can be so adjusted as to cause the precipitation of the corpuscles. These solutions are isotonic. Without going into details, it may be said that the isotonic coefficients obtained by Hamburger, agree well with those obtained by the plasmolytic method.

---

* Zeit. phys. Chem., **6**, 319 (1890).

The Hæmatocrit Method. In this method developed by Hedin,* advantage is again taken of the properties of red blood corpuscles. As has already been stated, when red blood corpuscles are immersed in solutions of gradually diminishing concentration of the same solute, they continue to swell and ultimately the semi-permeable envelope bursts. On the other hand, when the corpuscles are immersed in solutions of gradually increasing concentration, they shrink, owing to the transfer of water from the corpuscles. It is apparent that there must be a certain concentration for each solute which will cause no change in the volume of the corpuscles. To determine this concentration, use is made of an instrument known as an *hæmatocrit*. This is simply a graduated thermometer-tube which may be attached to the spindle of a centrifugal machine. When the spindle is revolved at high speed, the corpuscles collect in the bottom of the graduated tube. A measured volume of blood is centrifuged until no further shrinkage in volume of the corpuscles can be detected in the hæmatocrit. The same volume of blood is then added to each of a series of solutions whose concentration diminishes progressively, and the volume of the corpuscles is determined as in pure blood. In this way the concentration of the solution is found, in which the volume of the corpuscles is the same as in the undiluted blood. By proceeding in a similar manner with solutions of different substances, a series of isotonic coefficients can be determined. The following table gives a comparison of the isotonic coefficients of various substances obtained by the plasmolytic, blood corpuscle and hæmatocrit methods. The isotonic coefficients are referred to that of cane sugar as unity.

There are other methods which may be used for the comparison of osmotic pressures, among which may be mentioned that due to Wladimiroff,† involving the use of bacteria, and the interesting

---

* Ibid., 17, 164 (1895).

† Zeit. phys. Chem., 7, 529 (1891).

Substance.	Plasmolytic Method.	Corpuscle Method.	Hæmatocrit Method.
$C_{12}H_{22}O_{11}$	1.00	1.00	1.00
$MgSO_4$	1.09	1.27	1.10
KNO_3	1.67	1.74	1.84
$NaCl$	1.69	1.75	1.74
$CH_3.COOK$	1.67	1.66	1.67
$CaCl_2$	2.40	2.36	2.33

method developed by Tammann,* in which artificially prepared membranes are employed.

Osmotic Pressure and Diffusion. That there is a very close connection between osmotic pressure and diffusion, has already been pointed out. In fact the osmotic pressure of a solution may be regarded as the driving force which causes the molecules of a dissolved substance to distribute themselves uniformly throughout the solution.

The process of diffusion was first systematically investigated by Graham † in 1850, but it was not until five years later that the general law of diffusion was enunciated by Fick.‡ He proved theoretically and experimentally that the quantity of solute, ds, which diffuses through an area A, in a time dt, when the concentration changes by an amount dc, in a distance dx, at right angles to the plane of A, is given by the equation

$$ds = -DA\frac{dc}{dx}dt,$$

in which D is a constant, known as the *coefficient of diffusion*. Interpreting the equation of Fick in words, we see that the coefficient of diffusion is the amount of solute which will cross 1 square centimeter in 1 second, if the change of concentration per centimeter is unity.

The phenomena of diffusion have also been investigated by

---

* Wied. Ann., **34**, 299 (1888).

† Phil. Trans. (1850), p. 1, 805; (1851), p. 483.

‡ Pogg. Ann., **94**, 59 (1855).

Nernst * and Planck.† If we have a tall cylindrical vessel containing a solution of a non-electrolyte in its lower part, and pure water at the top, the solute will slowly diffuse upward into the water.

Assuming the osmotic pressure at a height x, to be P, and letting A denote the area of cross-section of the cylinder, the solute in the layer whose volume is $A\,dx$, will be subjected to a force equal to $-A\,dP$, the negative sign indicating that the force acts in the direction of diminishing pressure. If c is the concentration in mols per cubic centimeter, the force acting on each molecule in this layer will be

$$-\frac{A}{cA}\cdot\frac{dP}{dx} = -\frac{1}{c}\cdot\frac{dP}{dx}.$$

Let F denote the force necessary to drive a single molecule through the solution with the velocity of one centimeter per second. Since the velocity is constant, the resistance due to the viscosity of the medium must also be denoted by F. The velocity attained will be

$$-\frac{1}{cF}\cdot\frac{dP}{dx}.$$

If dN represents the number of molecules crossing each layer in a time dt, then, since the number crossing unit area per second is proportional to the concentration and to the mean velocity of the molecules, we shall have

$$dN = -\frac{1}{cF}\cdot\frac{dP}{dx}Ac\,dt,$$

or,

$$dN = -\frac{1}{F}A\frac{dP}{dx}dt.$$

When the solution is dilute, we may apply the general equation, $PV = RT$, remembering that $V = 1/c$. Substituting in the preceding equation, we have

$$dN = -\frac{RT}{F}A\frac{dc}{dx}dt.$$

---

* Zeit. phys. Chem., 2, 40, 615 (1888); 4,129 (1889).

† Wied. Ann., 40, 561 (1890).

Comparing this equation with that of Fick, we see that the coefficient of diffusion D, corresponds to the factor, RT/F. From the equation of Nernst it is possible to calculate the force required to drive a molecule of solute through the solution with unit velocity. Thus, solving the above equation for F, we have

$$F = -\frac{RT}{dN} A \frac{dc}{dx} dt.$$

By means of this equation, it has been calculated that the force necessary to drive one molecule of formic acid through water with a velocity of one centimeter per second at 0° C. is equal to the weight of 4,340,000,000 kilograms. It is difficult at first to realize that such enormous forces are operative in solutions, but when one considers the minute size of the molecules and the great resistance offered by the medium, it becomes evident that a very large driving force must be applied to produce an appreciable movement of the solute through the solution.

Principle of Soret. If a solution is maintained at a uniform temperature it will ultimately become homogeneous; if, on the other hand, two parts of a homogeneous solution are kept at different temperatures for some time, the solution will become more concentrated in the colder portion. This phenomenon was first investigated by Soret.* The experiments of Soret are of special interest, since they furnish a means of determining the influence of temperature on osmotic pressure. Thus, if the law of Gay-Lussac holds for osmotic pressure, the colder portion of a solution should increase in concentration by 1/273 for each degree of difference in temperature. The experimental results are in satisfactory agreement with the requirements of theory, and constitute another proof of the applicability of the gas laws to dilute solutions.

Lowering of Vapor Pressure. It has long been known that the vapor pressure of a solution is less than that of the pure solvent, provided the solute is non-volatile. The investigations of von Babo and Wüllner † on the lowering of vapor pressure of various liquids when non-volatile substances are dissolved in them, resulted in the following generalizations: — (1) *The lowering of the vapor pressure of a solution is proportional to the amount of solute present*; and (2) *For the same solution, the lowering of the vapor pressure of the solvent by a non-volatile solute is at all temperatures a constant fraction of the vapor pressure of the pure solvent.*

---

* Ann. Chem. Phys. (5), **22**, 293 (1881).

† Pogg. Ann., **103**, 529 (1858).

In 1887, Raoult,[*] as the result of an exhaustive experimental investigation, enunciated the following laws: — (1) *When equimolecular quantities of different non-volatile solutes are dissolved in equal volumes of the same solvent, the vapor pressure of the solvent is lowered by a constant amount*; and (2) *The ratio of the observed lowering of the vapor pressure to the vapor pressure of the pure solvent is equal to the ratio of the number of mols of solute to the total number of mols in the solution.* The ratio of the observed lowering to the original vapor pressure is called the *relative lowering of the vapor pressure.* Letting p_1 amd p_2 denote the vapor pressures of solvent and solution, Raoult's second law may be put in the form

$$\frac{p_1 - p_2}{p_1} = \frac{n}{N + n},$$

in which n and N represent the number of mols of solute and solvent respectively. Some of Raoult's results for ethereal solutions are given in the accompanying table.

Substance.	Mols of Solute per 100 mols of Solution.	$\frac{p_1 - p_2}{p_1}$ for Solution.	$\frac{p_1 - p_2}{p_1}$ for 1 molar per cent Solution.
Turpentine	8.95	0.0885	0.0099
Methyl salicylic acid	2.91	0.026	0.0089
Methyl benzoic acid	9.60	0.091	0.0095
Benzoic acid	7.175	0.070	0.0097
Trichloracetic acid	11.41	0.120	0.0105
Aniline	7.66	0.081	0.0106

The results given in the fourth column of the table are nearly constant, and are in close agreement with the theoretical value of the relative lowering of a 1 molar per cent solution calculated as follows: —

---

[*] Compt. rend., **104**, 1430 (1887); Zeit. phys. Chem., **2**, 372 (1888); Ann. Chem. Phys. (6), **15**, 375 (1888).

$$\frac{p_1 - p_2}{p_1} = \frac{1}{100 + 1} = 0.0099.$$

When the solution is very dilute, the number of mols of solute is negligible in comparison with the number of mols of solvent, and the equation of Raoult may be written

$$\frac{p_1 - p_2}{p_1} = \frac{n}{N}.$$

Since $n = g/m$, and $N = W/M$, where g and W are the weights of solute and solvent respectively, and m and M are the corresponding molecular weights, the above equation becomes

$$\frac{p_1 - p_2}{p_1} = \frac{gM}{Wm}.$$

This equation enables us to calculate the molecular weight of a dissolved substance from the relative lowering of the vapor pressure produced by the solution of a known weight of solute in a known weight of solvent. Solving the equation for m, we have

$$m = \frac{gM}{W} \cdot \frac{p_1}{p_1 - p_2}.$$

As an illustration of the application of this equation, we may take the determination of the molecular weight of ethyl benzoate from the following experimental data: — The vapor pressure at 80° C. of a solution of 2.47 grams of ethyl benzoate in 100 grams of benzene is 742.6 mm.: the vapor pressure of pure benzene at 80° C. is 751.86 mm. Substituting in the equation, we have

$$m = \frac{2.47 \times 78}{100} \cdot \frac{751.86}{751.86 - 742.6} = 156.$$

The molecular weight calculated from the formula, $C_6H_5COO.C_2H_5$, is 150.

The difficulties which attend the accurate measurement of the vapor pressure of a solution by the static method have already mentioned. While there are other methods which are pref-le for the determination of the molecular weight of dissolved tances, the vapor pressure method has one marked advan-, — it can be used for the same solution at widely divergent peratures. The method devised by Walker and already ribed in connection with the determination of the vapor sure of pure liquids (p. 92) is well adapted to the measure-t of the vapor pressure of solutions.

onnection between Lowering of Vapor Pressure and Osmotic ssure. The relation between osmotic pressure and the ering of vapor pressure has been derived the following manner by Arrhenius.[*] gine a very dilute solution contained in wide glass tube A, Fig. 64. The tube, s closed at its lower end with a semi-neable membrane, and dips into a vessel, which contains the pure solvent. The re apparatus is covered by a bell-jar C, the enclosed space exhausted. Let be the difference in level between the ent and solution when equilibrium is blished, that is, when the hydrostatic sure of the column of liquid is equal to osmotic pressure. When equilibrium is ined, the vapor pressure of the solution will be equal to the vapor pressure of solvent at this height. If the vapor pressure of the pure sol-t is p_1, and p_2 is the vapor pressure of the solution at h, we l have

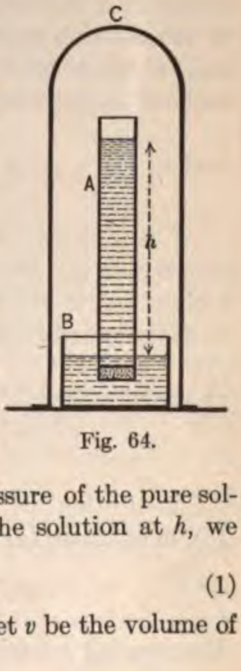


Fig. 64.

$$p_1 - p_2 = hd, \qquad (1)$$

re d denotes the density of the vapor. Let v be the volume of ol of solvent in the state of vapor, then

$$p_1 v = RT,$$

$$v = \frac{RT}{p_1}.$$

---

[*] Zeit. phys. Chem., 3, 115 (1889).

If the molecular weight of the solvent is M, we may replace v by M/d, when the preceding equation becomes

$$\frac{M}{d} = \frac{RT}{p_1},$$

or,

$$d = \frac{Mp_1}{RT}. \tag{2}$$

The solution being very dilute the osmotic pressure may be calculated from the equation

$$PV = nRT,$$

where P is the osmotic pressure of the solution, V the volume of the solution containing 1 mol of solute, and n the number of mols of solute present. If s represents the density of the solvent and also of the solution, since it is very dilute, we may write

$$P = hs,$$

and

$$V = \frac{g}{s},$$

where g is the number of grams of the solvent in which the n mols of solute are dissolved. Substituting these values of P and V in the general equation, we have

$$PV = nRT = hg,$$

and solving for h,

$$h = \frac{nRT}{g}. \tag{3}$$

Substituting the values of d and h, given in equations (2) and (3), in equation (1) we have

$$p_1 - p_2 = \frac{nRT}{g} \cdot \frac{Mp_1}{RT} = \frac{nMp_1}{g}. \tag{4}$$

Rearranging equation (4), and remembering that $N = g/M$, we obtain

$$\frac{p_1 - p_2}{p_1} = \frac{n}{N}. \tag{5}$$

This equation it will be seen, is identical with that derived experimentally by Raoult for very dilute solutions.

Van't Hoff showed, by an application of thermodynamics to dilute solutions, that the relation between osmotic pressure and the relative lowering of the vapor pressure is expressed by the equation

$$\frac{p_1 - p_2}{p_1} = \frac{MP}{sRT},$$

in which the symbols have the same significance as above. This equation may be reconciled easily with the equation of Raoult.

If n in equation (5) be replaced by its equal, PV/RT, the equation becomes

$$\frac{p_1 - p_2}{p_1} = \frac{PV}{NRT}.$$

But $V = NM/s$, hence

$$\frac{p_1 - p_2}{p_1} = \frac{MP}{sRT}.$$

This equation shows that the relative lowering of the vapor pressure is directly proportional to the osmotic pressure.

Elevation of the Boiling-Point. Just as the vapor pressure of a solution is less than that of the pure solvent, so the boiling-point of a solution is correspondingly higher than the boiling-point of the solvent. It follows that when equimolecular quantities of different substances are dissolved in equal volumes of the same solvent, the elevation of the boiling-point is constant. Thus, the molecular weight of any soluble substance may be determined by comparing its effect on the boiling-point of a particular solvent, with that of a solute of known molecular weight. The elevation in boiling-point produced by dissolving 1 mol of a solute in 100 grams, or 100 cubic centimeters, of a solvent is termed the *molecular elevation*, or *boiling-point constant* of the solvent. In determining the boiling-point constant of a solvent, a fairly dilute solution is employed and the elevation in the boiling-point is observed; the value of the constant is then calculated on the assumption that the elevation in boiling-point is proportional to the concentration.

If g grams of a substance of unknown molecular weight m, are dissolved in W grams of solvent, and the boiling-point is raised

Δ degrees, then, since m grams of the substance when dissolved in 100 grams of solvent, produce an elevation of K degrees (the molecular elevation), it follows that

$$\frac{100\,g}{W} : \Delta :: m : K,$$

therefore,

$$m = 100\,K\,\frac{g}{W\Delta}.$$

The accompanying table gives the boiling-point constants for 100 grams and 100 cubic centimeters of some of the more common solvents.

Solvent.	Molecular Elevation.	
	100 gr.	100 cc.
Water	5.2	5.4
Ethyl alcohol	11.5	15.6
Ether	21.0	30.3
Acetone	16.7	22.2
Benzene	26.7	32.8
Chloroform	35.6	....
Pyridine	30.1	....

As an example of the calculation of the molecular weight of a dissolved substance by the above formula, we may take the calculation of the molecular weight of camphor in acetone from the following data: —

When 0.674 gram of camphor is dissolved in 6.81 grams of acetone, the boiling-point of the solvent is raised 1°.09. Substituting in the formula, we have

$$m = 100 \times 16.7 \times \frac{0.674}{6.81 \times 1.09} = 151.$$

The molecular weight of camphor according to the formula $C_{10}H_{16}O$, is 152.

The molecular elevation of the boiling-point can be calculated by means of the formula,

$$K = \frac{0.02\,T^2}{w},$$

in which T is the absolute boiling-point of the solvent, and w is the heat of vaporization for 1 gram of the solvent at its boiling-point. This formula will be derived in a subsequent paragraph of this chapter. The calculated values of K are in close agreement with the values obtained experimentally by Raoult and others. As an example, the calculated value of the molecular elevation for water, the heat of vaporization of which at 100° C. is 537 calories, is

$$K = \frac{0.02 \times (373)^2}{537} = 5.2,$$

a value in exact agreement with the experimental value given in the table.

Experimental Determination of Molecular Weight by the Boiling-Point Method. One of the simplest and most convenient of the various forms of apparatus which have been devised for the determination of the boiling-point of solutions, is that developed by Jones,* and shown in Fig. 65. The liquid whose boiling-point is to be determined is introduced into the vessel A, which already contains a platinum cylinder P, embedded in some glass beads. Sufficient liquid is introduced to insure the complete covering of the bulb of the thermometer, as shown in the sketch.

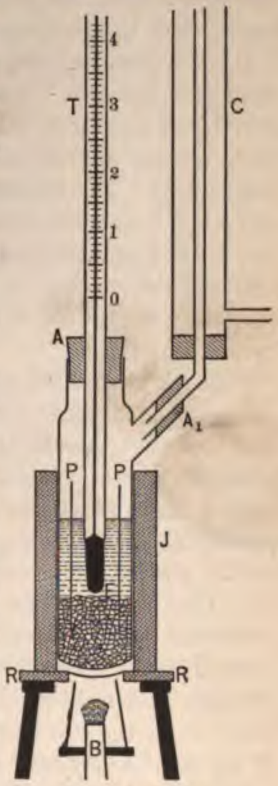


Fig. 65.

The side tube of A is connected with a condenser, C. The vessel A, is surrounded by a thick jacket of asbestos J, and rests on a piece of asbestos board in which a circular hole is cut, and over which a piece of wire gauze is placed. The liquid is heated by means of a burner, B. The platinum cylinder is the feature which differentiates this apparatus from the various other forms of boiling-point apparatus. It has the two-fold object of preventing the condensed solvent from coming in direct contact with the bulb of the thermometer, and of reducing the effect of radiation to a minimum. The liquid in A is boiled, using a very small flame, until the thermometer remains constant; this temperature is taken as the boiling-point of the liquid. The apparatus is now emptied and dried. A weighed amount of the liquid is then introduced into A, and to this is added a known weight of solute; the thermometer is replaced and the boiling-point of the solution is determined. The difference between the readings of the thermometer when immersed in the solution, and in the solvent alone, gives the boiling point elevation. For further details concerning the boiling-point method as applied to the determination of molecular weights, the student is referred to any one of the standard laboratory manuals.

---

* Am. Chem. Jour., 19, 581 (1897).

Osmotic Pressure and Boiling-Point Elevation. Imagine a dilute solution containing n mols of solute in G grams of solvent, and let dT be the elevation in the boiling-point. Suppose a large quantity of the solution to be introduced into a cylinder, fitted with a frictionless piston, and closed at the bottom by a semi-permeable membrane. Let the cylinder and contents be raised to the absolute temperature $T°$, the boiling-point of the solvent, and then let pressure be exerted on the piston just sufficient to overcome the osmotic pressure of the solution. In this way, let a quantity of solvent corresponding to 1 mol of solute be forced through the semi-permeable membrane. The volume V, thus expelled is the volume corresponding to G/n grams of solvent. If the osmotic pressure of the solution is P, then the work done in moving the piston and expelling the solvent is PV. Now let the portion of the solvent which has been forced through the semi-permeable membrane be vaporized. For this operation $G/n \,.\, w$ calories will be required, w being the heat of vaporization for 1 gram of solvent at its boiling-point. Then let the entire system be raised to the boiling-point of the solution $(T + dT)°$, the previously expelled G/n grams of vapor being allowed to mix with the solution. The heat of vaporization lost at $T°$ is thus recovered at the slightly higher temperature, $(T + dT)°$. Finally, the entire system is cooled to $T°$, and is thus restored to its original state. Applying the well-known thermodynamic relation, that the ratio of the work done to the heat absorbed, is the same as the ratio of the difference in temperature to the absolute initial temperature of the system, we have

$$\frac{PV}{\frac{G}{n} \cdot w} = \frac{dT}{T},$$

therefore,

$$dT = \frac{PVT}{w} \cdot \frac{n}{G}. \qquad (1)$$

But, since $PV = RT$, equation (1) may be written

$$dT = \frac{RT^2}{w} \cdot \frac{n}{G}.$$

If $n = 1$ and $G = 100$ grams, then $dT = K$, (the molecular elevation of the boiling-point), or

$$K = \frac{RT^2}{100\,w}.$$

Or putting $R = 2$ calories, we have

$$K = \frac{0.02\,T^2}{w}. \qquad (2)$$

Equation (1) shows that *the osmotic pressure of a solution is directly proportional to the elevation of the boiling-point.* Equation (2) was originally derived by van't Hoff at about the time when Raoult determined the values of K experimentally.

Lowering of the Freezing-Point. Of all the methods employed for the determination of molecular weights in solution, the freezing-point method is the most accurate and the most widely used. It was pointed out by Blagden * over a century ago, that *the depression of the freezing-point of a solvent by a dissolved substance is directly proportional to the concentration of the solution.* When equimolecular quantities of different substances are dissolved in equal volumes of the same solvent, the lowering of the freezing-point is constant. The molecular weight of any soluble substance can be found, as in the boiling-point method, by comparing its effect on the freezing-point of a solvent with that of a solute of known molecular weight. *The molecular lowering of the freezing-point, or the freezing-point constant, of a solvent is defined as the depression of the freezing-point produced by dissolving* 1 *mol of solute in* 100 *grams or* 100 *cubic centimeters of solvent.* The freezing-point constants of a few common solvents are given in the following table.

---

* Phil. Trans., **78**, 277 (1788).

Solvent.	Molecular Depression.	
	100 gr.	100 cc.
Water	18.5	18.5
Benzene	50	56
Phenol	74	....
Naphthalene	69	....
Acetic acid	39	41

Van't Hoff showed that the molecular lowering of the freezing-point of a solvent K, can be calculated from the absolute freezing-point T, and the heat of fusion w, for 1 gram of solvent at the temperature T, by means of the formula

$$K = \frac{0.02\,T^2}{w}.$$

This expression is analogous to that which applies to the molecular elevation of the boiling-point. The agreement between the observed and the calculated values of K is very satisfactory, as the following calculation for water shows: —

$$K = \frac{0.02 \times (273)^2}{80} = 18.6.$$

It is of interest to note that the calculated value of K for water is lower than the experimental values originally obtained by Raoult and others. Subsequent experiments, carried out with greater care and better apparatus, by Raoult, Abegg and Loomis gave values in close agreement with that derived theoretically. A formula analogous to that employed for the calculation of the molecular weight of a dissolved substance from the elevation it produces in the boiling-point of a solvent, may be used for the calculation of molecular weight from freezing-point depression. Thus, if g grams of solute when dissolved in W grams of solvent produce a depression Δ of the freezing-point of the solvent, the molecular weight m, is given by the formula

$$m = 100\,K \cdot \frac{g}{\Delta W},$$

where K is the molecular lowering of the freezing-point.

Example. When 1.458 grams of acetone are dissolved in 100 grams of benzene, the freezing-point of the solvent is depressed 1.22°, therefore the molecular weight of acetone is

$$m = 100 \times 50 \times \frac{1.458}{1.22 \times 100} = 59.8.$$

The molecular weight of acetone, calculated from the formula C_3H_6O, is 58.

In order to obtain trustworthy results with the freezing-point method, it is necessary that only the pure solvent separate out when the solution freezes, and that excessive overcooling be avoided. When too great overcooling occurs, the subsequent freezing of the solution results in the separation of so large an amount of solvent in the solid state, that the observed freezing point corresponds to the equilibrium temperature of a more concentrated solution than that originally prepared. A formula for the correction of the concentration, due to excessive overcooling, has been derived by Jones.* If the overcooling of the solution in degrees be represented by u, the heat of fusion of 1 gram of solvent at the freezing-point by w, and the specific heat of the solvent by c, then the fraction of the solvent which will solidify, f, may be calculated by the formula,

$$f = \frac{cu}{w}.$$

When water is used as the solvent, $c = 1$ and $w = 80$. Therefore, for every degree of overcooling, the fraction of the solvent separating as ice will be 1/80, and the concentration of the original solution is increased by just so much. It is simpler, however, to apply the correction directly to the freezing-point depression instead of to the concentration.

---

* Zeit. phys. Chem., **12**, 624 (1893).

Experimental Determination of Molecular Weight by the Freezing-Point Method. The apparatus almost universally employed for the determination of molecular weights by the freezing-point method is that devised by Beckmann,* and shown in Fig. 66. It consists of a thick-walled test tube *A*, provided with a side tube, and fitted into a wider tube A_1, thus surrounding *A* with an air space.

The whole is fitted into the metal cover of a large battery jar, which is filled with a freezing mixture whose temperature is several degrees below the freezing-point of the solvent.

The tube *A* is closed by a cork stopper, through which passes the thermometer and stirrer. The thermometer is generally of the Beckmann differential type. This instrument has a scale about 6° in length, each degree being divided into hundredths; the quantity of mercury in the bulb can be varied by means of a small reservoir at the top of the scale, so that the zero of the instrument can be adjusted for use with solvents of widely different freezing-points. In carrying out a determination with the Beckmann apparatus, a weighed quantity of solvent is placed in *A*, and the temperature of the refrigerating mixture regulated so as to be not more than 5° below the freezing-point of the solvent. The tube *A* is removed from its jacket, and is immersed in the freezing mixture until the solvent begins to freeze. It is then replaced in the jacket A_1, and the solvent is vigorously stirred. The thermometer rises during the stirring until the true freezing-point is reached, after which it remains constant. This temperature is taken as the freezing temperature of the solvent.

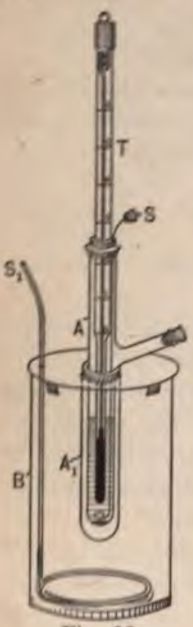


Fig. 66.

---

[*] Zeit. phys. Chem., 2, 683 (1888).

The tube A is now removed from the freezing mixture, and a weighed amount of the substance whose molecular weight is to be determined is introduced. When the substance has dissolved, the tube is replaced in A_1 and the solution cooled not more than a degree below its freezing-point. A small fragment of the solid solvent is dropped into the solution, which is then stirred vigorously until the thermometer remains constant. The maximum temperature is taken as the freezing-point of the solution. The difference between the freezing-points of solution and solvent is the depression sought. For further details concerning the determination of molecular weights by the freezing-point method, the student is referred to a physico-chemical laboratory manual.

Osmotic Pressure and Freezing-Point Depression. Let dT be the freezing-point depression produced by n mols of solute in G grams of solvent, the solution being dilute. Imagine a large quantity of this solution to be confined within a cylinder fitted with a frictionless piston, the bottom of the cylinder being closed by a semi-permeable membrane. Let the cylinder and contents be cooled to the freezing temperature of the solvent T, and then let pressure be applied to the piston until a quantity of solvent corresponding to 1 mol of solute is forced through the semi-permeable membrane. This requires an expenditure of energy equivalent to PV, where P is the osmotic pressure of the solution and V is the volume of solvent expelled. The volume V is clearly the volume of G/n grams of solvent. Now let the expelled portion of solvent be frozen and the system deprived of $\frac{G}{n}w$ calories of heat, where w is the heat of fusion of 1 gram of the solvent at the temperature T.

The temperature of the solution is then lowered to its freezing-point $(T - dT)$, and the G/n grams of solidified solvent dropped into it. The solidified solvent melts, thereby restoring to the system at the temperature $(T - dT)$, the heat of fusion formerly taken from it. Finally, the temperature of the system is raised to T, the initial temperature of the cycle. Applying the familiar thermodynamic relation, that the ratio of the work done to the heat absorbed, is the same as the ratio of the difference in temperature to the initial absolute temperature, we have

$$\frac{PV}{\frac{G}{n}w} = \frac{dT}{T}. \tag{1}$$

From which we obtain

$$dT = \frac{PVT}{w} \cdot \frac{n}{G}.$$

But $PV = RT$, hence equation (1) becomes

$$dT = \frac{RT^2}{w} \cdot \frac{n}{G}.$$

If $n = 1$ and $G = 100$ grams, then $dT = K$, the molecular lowering of the freezing-point, and

$$K = \frac{RT^2}{100\,W}.$$

Or putting $R = 2$ calories, we have

$$K = \frac{0.02\,T^2}{w}. \tag{2}$$

An equation to which reference has already been made.

It is evident from equation (1) that *the osmotic pressure of a solution is directly proportional to the freezing point depression.*

Molecular Weight in Solution. As has been pointed out, the molecular weight of a dissolved substance can be readily calculated, provided that the osmotic pressure of a dilute solution of known concentration at known temperature is determined. But the experimental difficulties attending the direct measurement of osmotic pressure are so great, that it is customary to employ other methods based upon properties of dilute solutions which are proportional to osmotic pressure. We have shown that in dilute solutions osmotic pressure is directly proportional (1) to the relative lowering of the vapor pressure, (2) to the elevation of the boiling-point, and (3) to the depression of the freezing-point.

From this it follows, that *equimolecular quantities of different substances dissolved in equal volumes of the same solvent, exert the* *same osmotic pressure, and produce the same relative lowering of vapor pressure, the same elevation of boiling-point, and the same depression of freezing-point. Since equimolecular quantities of different substances contain the same number of molecules, it is evident that the magnitude of osmotic pressure, relative lowering of vapor pressure, elevation of boiling-point and depression of freezing-point, is dependent upon the number of particles present in the solution and is independent of their nature.* It has been pointed out by Nernst that any process which involves the separation of solvent from solute, may be employed for the determination of molecular weights. A little reflection will convince the reader that the four methods discussed in this chapter involve such separation. Both van't Hoff and Raoult emphasized the fact that the formulas derived for the determination of molecular weights in solution depend upon assumptions which are valid only for dilute solutions. It follows, therefore, that *we are not justified in applying these formulas to concentrated solutions.* Up to the present time we have no satisfactory theory of concentrated solutions, neither can we state up to what concentration the gas laws apply.

PROBLEMS.

1. At 10° C. the osmotic pressure of a solution of urea is 500 mm. of mercury. If the solution is diluted to ten times its original volume, what is the osmotic pressure at 15° C.? *Ans.* 50.89 mm.

2. The osmotic pressure of a solution of 0.184 gram of urea in 100 cc. of water was 56 cm. of mercury at 30° C. Calculate the molecular weight of urea. *Ans.* 62.12.

3. At 24° C. the osmotic pressure of a cane sugar solution is 2.51 atmospheres. What is the concentration of the solution in mols per liter? *Ans.* 0.103.

4. At 25°.1 C. the osmotic pressure of solution of glucose containing 18 grams per liter was 2.43 atmospheres. Calculate the numerical value of the constant R, when the unit of energy is the gram-centimeter. *Ans.* 84,231.

5. The vapor pressure of ether at 20° C. is 442 mm. and that of a solution of 6.1 grams of benzoic acid in 50 grams of ether is 410 mm. at the same temperature. Calculate the molecular weight of benzoic acid in ether. *Ans.* 124.

6. At 10° C. the vapor pressure of ether is 291.8 mm. and that of a solution containing 5.3 grams of benzaldehyde in 50 grams of ether is 271.8 mm. What is the molecular weight of benzaldehyde?

Ans. 106.6.

7. A solution containing 0.5042 gram of a substance dissolved in 42.02 grams of benzene boils at 80°.175 C. Find the molecular weight of the solute, having given that the boiling-point of benzene is 80°.00 C., and its heat of vaporization is 94 calories per gram. *Ans.* 181.9.

8. A solution containing 0.7269 grams of camphor (mol. wt. = 152) in 32.08 grams of acetone (boiling-point = 56°.30 C.) boiled at 56°.55 C. What is the molecular elevation of the boiling-point of acetone? What is its heat of vaporization?

Ans. $K = 16.74$; $w = 129.5$ cals. per gm.

9. A solution of 9.472 grams of CdI_2 in 44.69 grams of water boiled at 100°.303 C. The heat of vaporization of water is 536 calories per gram. What is the molecular weight of CdI_2 in the solution? What conclusion as to the state of CdI_2 in solution may be drawn from the result?

Ans. 363.2.

10. The freezing-point of pure benzene is 5°.440 C. and that of a solution containing 2.093 grams of benzaldehyde in 100 grams of benzene is 4°.440 C. Calculate the molecular weight of benzaldehyde in the solution. K for benzene is 50. *Ans.* 104.6.

11. A solution of 0.502 gram of acetone in 100 grams of glacial acetic acid gave a depression of the freezing-point of 0°.339 C. Calculate the molecular depression for glacial acetic acid. *Ans.* 39.

12. By dissolving 0.0821 gram of m-hydroxybenzaldehyde ($C_7H_6O_2$) in 20 grams of naphthalene (melting point 80°.1 C.) the freezing-point is lowered by 0°.232 C. Assuming that the molecular weight of the solute is normal in the solution, calculate the molecular depression for naphthalene and the heat of fusion per gram.

Ans. $K = 68.96$; $w = 36.2$ cals. per gm.

CHAPTER XI.

ASSOCIATION, DISSOCIATION AND SOLVATION.

Abnormal Solutes. As has already been pointed out the acceptance of Avogadro's hypothesis was greatly retarded by the discovery of certain substances whose vapor densities were abnormal. Thus, the vapor density of ammonium chloride is approximately one-half of that required by the formula NH_4Cl, while the vapor density of acetic acid corresponds to a formula whose molecular weight is greater than that calculated from the formula, $C_2H_4O_2$. The anomalous behavior of ammonium chloride and kindred substances has been shown to be due, not to a failure of Avogadro's law, but to a breaking down of the molecules, — a process known as *dissociation*. The abnormally large molecular weight of acetic acid on the other hand, has been ascribed to a process of aggregation of the normal molecules, known as *association*. In extending the gas laws to dilute solutions similar phenomena have been encountered.

Association in Solution. When the molecular weight of acetic acid in benzene is determined by the freezing-point method, the depression of the freezing-point is abnormally small and consequently, as the formula

$$m = 100\,K\,\frac{g}{\Delta W},$$

shows, the molecular weight will be greater than that corresponding to the formula, $C_2H_4O_2$. Acetic acid in benzene solution is thus shown to be associated. Almost all compounds containing the hydroxyl and cyanogen groups when dissolved in benzene are found to be associated. Solvents, such as benzene and chloroform, are frequently termed associating solvents, although it is doubtful whether they exert any associating action. There is considerable experimental evidence to show that those substances whose molecules are associated in benzene and chloroform solution, are also associated in the free condition. Just as the depression of the freezing-point of a solution of an associated substance is abnormally small, so its osmotic pressure and other related properties will be less than the calculated values.

Dissociation in Solution. Van't Hoff * pointed out that the osmotic pressure of solutions of most salts, of all strong acids, and of all strong bases is much greater for all concentrations than would be expected from the osmotic pressure of solutions of substances, like cane sugar or urea, for corresponding concentrations. He was unable to account for this abnormal behavior, and in order to render the general gas equation applicable, he introduced a factor i, the modified equation being

$$PV = iRT.$$

If the osmotic pressure of some substance, like cane sugar, which behaves normally, be represented by P_0, the factor i is given by the expression

$$i = \frac{P}{P_0}.$$

Since the osmotic pressure of a solution is proportional to the relative lowering of its vapor pressure, to the elevation of its boiling-point, and to the lowering of its freezing-point, we may write

$$i = \frac{P}{P_0} = \frac{\dfrac{p_1 - p_2}{p_1}}{\dfrac{p_1 - p_0}{p_1}} = \frac{\Delta}{\Delta_0},$$

where the symbols have their usual significance. The subscript 0 refers in each case to a substance which behaves normally, and Δ denotes either boiling-point elevation or freezing-point depression. A more definite conception of the abnormal behavior of salts will be gained by an inspection of the accompanying tables. In the first column is recorded the molar concentration of the solution; the second column gives the observed depressions of the freezing-point and the third column contains the values of the ratio of the observed depression to the normal depression, or i.

---

* Zeit. phys. Chem., 1, 501 (1887).

POTASSIUM CHLORIDE.

m	Δ	i
0.05	0.1750	1.88
0.10	0.3445	1.85
0.20	0.6808	1.83
0.40	1.3412	1.80

POTASSIUM SULPHATE.

m	Δ	i
0.05	0.2270	2.33
0.10	0.4317	2.32
0.20	0.8134	2.18
0.30	1.1673	2.09

ALUMINIUM CHLORIDE.

m	Δ	i
0.046	0.276	3.22
0.076	0.446	3.15
0.102	0.578	3.04
....	....	....

SODIUM CHROMATE.

m	Δ	i
0.1	0.450	2.42
0.2	0.850	2.28
0.5	1.960	2.11
1.0	3.800	2.04

It is apparent from the above data that the depression of the freezing-point of water caused by these salts is abnormally large, a fact which points to an increase in the number of dissolved units over that corresponding to the initial concentration.

The Theory of Electrolytic Dissociation. In 1887, Arrhenius * advanced an hypothesis to account for the abnormal osmotic activity of solutions of acids, bases and salts. He pointed out that just as the exceptional behavior of certain gases has been completely reconciled with the law of Avogadro, by assuming a dissociation of the vaporized molecule into two or more simpler molecules, so the enhanced osmotic pressure and the abnormally great freezing-point depression of solutions of acids, bases and salts can be explained, if we assume a similar process of dissociation. He proposed, therefore, that aqueous solutions of acids, bases and salts be considered as dissociated, to a greater or less extent, into positively- and negatively-charged particles or *ions*, and that the increase in the number of dissolved units due to this dissociation is the cause of the enhanced osmotic activity. According to this hypothesis, hydrochloric acid, potassium hydroxide and potassium chloride, when dissolved in water, dissociate in the following manner: —

---

* Zeit. phys. Chem., 1, 631 (1887).

$$HCl \rightarrow H^{\cdot} + Cl'$$
$$KOH \rightarrow K^{\cdot} + OH'$$
$$KCl \rightarrow K^{\cdot} + Cl',$$

where the dots indicate positively-charged ions and the dashes negatively-charged ions.

In each of the above cases, one molecule yields two ions, so that, if dissociation is complete, the maximum osmotic effect should not be greater than twice that produced by an equimolecular quantity of a substance which behaves normally. Reference to the preceding table shows that the value of i for potassium chloride approaches the limiting value of 2 as the solution is diluted. The other salts given in the table dissociate, according to Arrhenius, in the following way: —

$$K_2SO_4 \rightarrow 2\,K^{\cdot} + SO_4''$$
$$Na_2CrO_4 \rightarrow 2\,Na^{\cdot} + CrO_4''$$
$$AlCl_3 \rightarrow Al^{\cdot\cdot\cdot} + 3\,Cl'.$$

If these equations correctly represent the process of dissociation, then when dissociation is complete, the osmotic effect of infinitely dilute solutions of potassium sulphate and sodium chromate should be three times the effect produced by an equimolecular quantity of a normal solute, and in the case of aluminium chloride, the maximum effect should be four times the effect due to a normal substance. A glance at the table shows that the values of i for solutions of the three salts approach these respective limits. If this hypothesis of ionic dissociation be accepted, then it becomes possible to calculate the degree of ionization in any solution by comparing its freezing-point depression with the freezing-point lowering of an equimolecular solution of a normal substance.

Let us suppose that the degree of dissociation of 1 molecule of a dissolved substance is α, each molecule yielding n ions. Then

$1 - \alpha$ will be the undissociated portion of the molecule, and the total number of dissolved units will be

$$1 - \alpha + n\alpha.$$

If Δ is the depression of the freezing-point produced by the substance, and Δ_0 the depression produced by an equimolecular quantity of an undissociated substance, then

$$\frac{1 - \alpha + n\alpha}{1} = \frac{\Delta}{\Delta_0} = i,$$

or

$$\alpha = \frac{i - 1}{n - 1}.$$

It will be observed that this formula is identical with that derived for the degree of dissociation of a gas (p. 91). If this formula be applied to the freezing-point data for solutions of potassium chloride given in the preceding table we find the following percentages of dissociation corresponding to the different concentrations: —

POTASSIUM CHLORIDE.

m	Δ	i	α %
0.05	0.1750	1.88	88
0.10	0.3445	1.85	85
0.20	0.6808	1.83	83
0.40	1.3412	1.80	80

The figures in the last column show that the degree of dissociation increases as the concentration diminishes. It was further pointed out by Arrhenius that all of the substances which exhibit abnormal osmotic effects, when dissolved in water, yield solutions which conduct the electric current, whereas, aqueous solutions of such substances as cane sugar, urea and alcohol, exert normal osmotic pressures, but do not conduct electricity any better than the pure solvent. In other words, only electrolytes[*] are capable of undergoing ionic dissociation; hence Arrhenius termed his hypothesis the *electrolytic dissociation theory*. As we have seen, when potassium chloride is dissolved in water, it is supposed to dissociate into positively-charged potassium ions and negatively-charged chlorine ions. Accordingly when two platinum electrodes, one charged positively and the other negatively, are introduced into the solution, the potassium ions move toward the negative electrode and the chlorine ions move toward the positive electrode, the passage of a current through the solution consisting in the ionic transfer of electric charges. Since the undissociated molecules, being electrically neutral, do not participate in the transfer of electric charges, it follows that the conductance of a solution of an electrolyte is dependent upon the degree of dissociation. The relation between electrical conductance and the degree of ionization will be discussed in a subsequent chapter. It may be stated at this point, however, that the values of α based upon measurements of electrical conductance, while showing some discrepancies in individual cases, are in general in good agreement with the values obtained by the freezing-point method. Furthermore, the values of α obtained from freezing-point measurements are in harmony with those based upon De Vries' isotonic coefficients. It will be seen, on referring to the table of isotonic coefficients (p. 181), that solutions of electrolytes show enhanced osmotic activity. Thus, the osmotic pressures of equi-molecular solutions of cane sugar, potassium nitrate and calcium chloride are to each other as 1 : 1.67 : 2.40.

---

[*] The term *electrolyte* strictly refers to the solution of an ionized substance, although it is often applied to acids, bases and salts because, when dissolved, they produce electrolytes. To avoid confusion, the term "*ionogen*" (ion former) has been proposed for those substances which give conducting solutions.

The following table illustrates the general agreement between the values of i calculated, (a) from electrical conductance, (b) from freezing-point depression, and (c) from De Vries' isotonic coefficients.

Substance.	Molar Conc.	(a)	(b)	(c)
KCl	0.14	1.86	1.82	1.81
LiCl	0.13	1.84	1.94	1.92
$Ca(NO_3)_2$	0.18	2.46	2.47	2.48
$MgCl_2$	0.19	2.48	2.68	2.79
$CaCl_2$	0.184	2.42	2.67	2.78

It must be remembered that the values of i derived from freezing-point measurements correspond to temperatures in the neighborhood of 0° C., while those derived from the other methods correspond to temperatures ranging from 17° C. to 25° C.

Chemical Properties of Completely Ionized Solutions. The chemical properties of an ion are very different from the properties of the atom or radical when deprived of its electrical charge. For example, the sodium ion is present in an aqueous solution of sodium chloride, but there is no evidence of chemical reaction with the solvent; whereas, the element in the electrically-neutral condition reacts violently with water, evolving hydrogen and forming a solution of potassium hydroxide. Again, take the element chlorine: when chlorine in the molecular condition, either as gas or in solution, is added to a solution of silver nitrate, no precipitate of silver chloride is formed. Further, chlorine in such compounds as $CHCl_3$, CCl_4, etc., is not precipitated by silver nitrate, since these compounds are not dissociated by water. Or, chlorine may be present in a compound which is dissociated by water and yet not exhibit its characteristic reactions, because it is present in a complex ion. Thus, potassium chlorate dissociates in the following manner: —

$$KClO_3 \rightarrow K^{\cdot} + ClO_3'.$$

On adding silver nitrate, there is no precipitation, because the chlorine forms a complex ion with oxygen.

Physical Properties of Completely Ionized Solutions. The physical properties of completely ionized solutions are, in general, additive. This is well illustrated by a series of solutions of colored salts, the color of which is due to the presence of a particular ion. It is found, when the solutions are sufficiently dilute to insure complete dissociation, that they all have the same color. The additive character of the colors of solutions of electrolytes is brought out in a striking manner by a comparison of their absorption spectra. Ostwald * photographed the absorption spectra of solutions of the permanganates of lithium, cadmium, ammonium, zinc, potassium, nickel, magnesium, copper, hydrogen and aluminium, each solution containing 0.002 gram-equivalents of salt per liter. The absorption spectra, as shown in Fig. 67, will be seen to be practically identical, the bands occupying the same position in each spectrum. This affords a strong confirmation of the theory of electrolytic dissociation, according to which a dilute solution is to be regarded as a mixture of electrically equivalent quantities of oppositely charged ions, each of which contributes its specific properties to the solution. The permanganate ion being colored, and common to all of the salts examined, and the positive ions of the various substances being colorless, it follows that when dissociation is complete, the absorption spectra of all of the solutions must be identical. A number of other properties of completely dissociated solutions have been shown to be additive. Among these may be mentioned density, specific refraction, surface tension, thermal expansion, and magnetic rotatory power. Additional evidence in favor of the theory of electrolytic dissociation will be furnished in forthcoming chapters. Notwithstanding the large number of facts which can be satisfactorily interpreted by the theory, there are directions in which it requires amplification and modification. Of the various objections which have been urged against the theory of electrolytic dissociation, one is of sufficient weight to call for brief consideration here. When two elements, such as potassium and chlorine, combine to form potassium chloride, the reaction is violent and a large amount of heat is developed. Nevertheless,

---

* Zeit. phys. Chem., 9, 579 (1892).

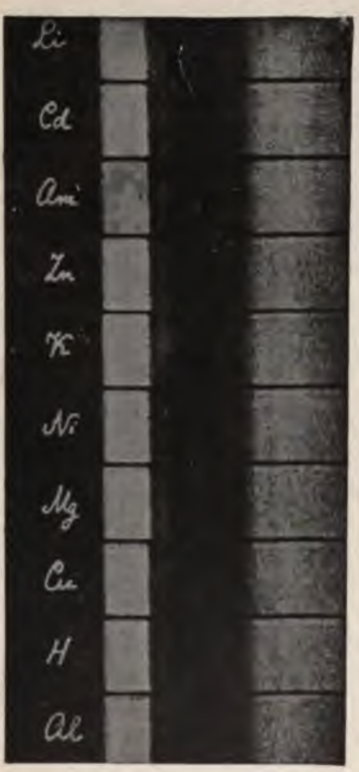


Fig. 67.

according to the ionization theory, the strong, mutual affinity of these two elements is overcome by the act of solution in water, the molecule being split into two oppositely-charged atoms. Obviously such a separation calls for the expenditure of a large amount of energy, and the question naturally arises: — What is the source of this energy? While this question cannot be fully answered here, it may be pointed out that we have abundant evidence to show that the ions are hydrated, each being surrounded by an "atmosphere" of solvent. In view of this fact, it has been suggested * that dissociation in aqueous solution is caused by the mutual attraction between the ions and the molecules of the solvent, the heat of ionic hydration furnishing the energy necessary for the separation of the ions.

Freezing-Point Depressions Produced by Concentrated Solutions of Electrolytes. As has already been mentioned, the dissociation of electrolytes in aqueous solution increases with the dilution, becoming complete at a concentration of about 0.001 molar. We should expect the dissociation to diminish with increasing concentration, until, if the electrolyte is sufficiently soluble, the depression of the freezing-point becomes normal. Recent investigations by Jones and his co-workers † have shown that the facts are contradictory to this expectation. They found that the value of the molecular depression of the freezing-point of water produced by a number of chlorides and bromides, diminished with increasing concentration up to a certain point, as would be expected, and then increased again. The increase in the molecular depression became very marked at great concentrations; in fact, the molecular depression in a molar solution was frequently greater than the molecular depression corresponding to a completely dissociated salt. This phenomenon was systematically studied by Jones and the author ‡ and the fact was established that it is quite general.

---

* Trans. Faraday Soc., **1**, 197 (1905); **3**, 123 (1907).

† Am. Chem. Jour., **22**, 5, 110 (1899); **23**, 89 (1900).

‡ Zeit. phys. Chem., **46**, 244 (1903); Phys. Rev., **18**, 146 (1904); Am. Chem. Jour., **31**, 303 (1904); **32**, 308 (1904); **33**, 534 (1905); **34**, 291 (1905); Zeit. phys. Chem., **49**, 385 (1904); Monograph No. 60, Carnegie Institution of Washington.

This abnormal depression of the freezing-point may be accounted for by assuming that the dissolved substance has entered into combination with a portion of the water, thus removing it from the rôle of solvent. The formation of a loose molecular complex between one molecule of the solute and a large number of molecules of water, acts as a single dissolved unit in depressing the freezing-point of the pure solvent. Evidently the total amount of water present, which functions as solvent, is diminished by the amount of water which has been appropriated by the solute. The abnormalities observed in the depression of the freezing-point of concentrated solutions of electrolytes can be explained by assuming that the molecules of solute, or the resulting ions, are in combination with a number of molecules of solvent. This hypothesis is termed the *solvate theory*, and the loose molecular complexes are called *solvates*. Since the solvate theory was first proposed, considerable evidence has been accumulated to confirm its correctness. Reference has already been made to the work of Philip on the solubility of gases in saline solutions, from which he concludes that the dissolved salts enter into combination with a portion of the solvent. The experiments of Morse and the Earl of Berkeley on osmotic pressure, also seem to point to the solvation of the dissolved substance.

PROBLEMS.

1. At 18° C. a 0.5 molar solution of NaCl is 74.3 per cent dissociated. What would be the osmotic pressure of the solution in atmospheres at 18° C.? *Ans.* 20.79.

2. A solution containing 3 mols of cane sugar per liter was found by the plasmolytic method to be isotonic with a solution of potassium nitrate containing 1.8 mols per liter. What is the degree of ionization of the potassium nitrate? *Ans.* 67 per cent.

3. The vapor pressure of water at 20° C. is 17.406 mm. and that of a 0.2 molar solution of potassium chloride is 17.296 mm. at the same temperature. Calculate the degree of dissociation of the salt. *Ans.* 75.38 per cent.

4. The degree of dissociation of a 0.5 molar solution of sodium chloride at 25° is 74.3 per cent. Calculate the osmotic pressure of the solution at the same temperature. *Ans.* 21.32 atmos.

5. A solution containing 1.9 mols of calcium chloride per liter is isotonic with a solution of glucose containing 4.05 mols per liter. What is the degree of ionization of the calcium chloride? *Ans.* 56.6 per cent.

6. At 0° C. the vapor pressure of water is 4.620 mm. and of a solution of 8.49 grams of $NaNO_3$ in 100 grams of water 4.483 mm. Calculate the degree of ionization of $NaNO_3$. *Ans.* 64.9 per cent.

7. At 0° C. the vapor pressure of water is 4.620 mm. and that of a solution of 2.21 grams of $CaCl_2$ in 100 grams of water is 4.583 mm. Calculate the apparent molecular weight and the degree of ionization of $CaCl_2$. *Ans.* $M = 49.66$, $\alpha = 62$ per cent.

8. The boiling-point of a solution of 0.4388 gram of sodium chloride in 100 grams of water is 100°.074 C. Calculate the apparent molecular weight of the sodium chloride and its degree of ionization. $K = 5.2$. *Ans.* $M = 30.84$, $\alpha = 89.7$ per cent.

9. The boiling-point of a solution of 3.40 grams of $BaCl_2$ in 100 grams of water is 100°.208 C. $K = 5.2$. What is the degree of ionization of the $BaCl_2$? *Ans.* 72.5 per cent.

10. At 100° C. the vapor pressure of a solution of 6.48 grams of ammonium chloride in 100 grams of water is 731.4 mm. $K = 5.2$. What is the boiling-point of the solution? *Ans.* 101°.086 C.

11. A solution of 1 gram of silver nitrate in 50 grams of water freezes at − 0°.348 C. Calculate to what extent the salt is ionized in solution. $K = 18.6$. *Ans.* 59 per cent.

12. A solution of NaCl containing 3.668 grams per 1000 grams of water freezes at − 0°.2207 C. Calculate the degree of ionization of the salt. $K = 18.6$. *Ans.* 89.2 per cent.

13. The freezing-point of a solution of barium hydroxide containing 1 mol in 64 liters is − 0°.0833 C. What is the concentration of hydroxyl ions in the solution? Take $K = 18.9$ for concentrations in mols per liter. *Ans.* 0.0284 gm.-ion per liter.

14. The vapor pressure of water at 0° C. is 4.620 mm., and the lowering of the vapor pressure produced by dissolving 5.64 grams of sodium chloride in 100 grams of water is 0.142 mm. What is the freezing-point of the solution? $K = 18.6$. *Ans.* − 3°.177 C.

15. A solution containing 8.34 grams Na_2SO_4 per 1000 grams of water freezes at − 0°.280 C. Assuming dissociation into 3 ions, calculate the

degree of ionization and the concentrations of the $Na^{\cdot}$ and SO_4'' ions. $K = 18.6$.

Ans. $\alpha = 78.2$ per cent; conc. $Na^{\cdot} = 0.0918$ gm.-ion per liter; conc. $SO_4'' = 0.0459$ gm.-ion per liter.

CHAPTER XII.

COLLOIDS.

Crystalloids and Colloids. In the course of his investigations on diffusion in solutions, Thomas Graham * drew a distinction between two classes of solutes, which he termed *crystalloids* and *colloids*. Crystalloids, as the name implies, can be obtained in the crystalline form: to this class belong nearly all of the acids, bases and salts. Colloids, on the other hand, are generally amorphous, such substances as albumin, starch and caramel being typical of the class. Because of the gelatinous character of many of the substances in this class, Graham termed them colloids (κολλα = glue, and ετδος = form). The differences between the two classes are most apparent in the physical properties of their solutions. Thus, crystalloids diffuse much more rapidly than colloids; the velocity of diffusion of caramel being nearly 100 times slower than that of hydrochloric acid at the same temperature. While crystalloids exert osmotic pressure, lower the vapor pressure and depress the freezing-point of the solvent, colloids have very little effect upon the properties of the solvent. The marked differences in the rates of diffusion of crystalloids and colloids render their separation comparatively easy. If a solution containing both crystalloids and colloids be placed in a vessel over the bottom of which is stretched a colloidal membrane, such as parchment, and the whole is immersed in pure water, the crystalloids will pass through the membrane, while the colloids will be left behind. This process was termed by Graham, *dialysis,* while the apparatus employed to effect such a separation was called a *dialyzer*. When a solution of sodium silicate is added to an excess of hydrochloric acid, the products of the reaction, silicic acid and sodium chloride, remain in solution. When the mixture is placed in a dialyzer, the sodium chloride and the hydrochloric acid, being crystalloids, diffuse through the membrane of the dialyzer, leaving behind the colloidal silicic acid.

---

* Lieb. Ann., 121, 1 (1862).

The terms crystalloid and colloid, as used at the present time, have acquired different meanings from those assigned to them by Graham. The terms are now considered to refer, not so much to different classes of substances, as to different states which almost all substances can assume under certain conditions.

Colloidal Solutions. A colloidal solution is one in which the solute is a colloid, although the latter may not be included among the substances classified as such by Graham. For example, arsenious sulphide, ferric hydroxide or finely-divided gold may form colloidal solutions. In bringing such substances into the colloidal state, mere agitation with water will not suffice, but some indirect method must be employed.

Nomenclature. Graham distinguished between two conditions in which colloids were obtainable, the term *sol* being applied to forms in which the system resembled a liquid, while the term *gel* was used to designate those forms which were solid and jelly-like. When one of the components of the solution was water, the two forms were called a *hydrosol* and a *hydrogel*. In like manner, when alcohol was one of the components, the terms *alcosol* and *alcogel* were applied to the two forms.

As the knowledge of colloids has developed it has become necessary to supplement Graham's nomenclature by the introduction of various other terms. It is known to-day that the essential difference between colloidal suspensions and solutions on the one hand, and true solutions on the other, is due to the difference in the degree of subdivision or degree of *dispersity* of the dissolved substance. In a true solution the dissolved substance is generally present either in the molecular or ionic condition, as may be shown by means of the familiar osmotic methods for molecular weight determination. In colloidal solutions, however, the degree of dispersity is not so great and has been found to vary from above the limit of microscopic visibility (1×10^{-5} cm.) to that of molecular dimensions (1×10^{-8} cm.). When the degree of dispersity varies from 1×10^{-3} cm. to 1×10^{-5} cm. the particles are termed *microns*. The properties of the disperse phase at this degree of dispersity differ appreciably from the properties of the same substance when present in large masses. When the degree of dispersity lies between 1×10^{-5} cm. and 5×10^{-7} cm. the particles are known as *submicrons*. The existence of particles whose diameters are approximately 1×10^{-7} cm. has been demonstrated by Zsigmondy with the ultramicroscope; these minute particles are termed *amicrons*. When the degree of dispersity is increased beyond this limit all heterogeneity apparently vanishes and we enter the realm of true solutions.

When the dispersion is not too great, colloidal solutions may be divided into *suspensions* and *emulsions* according to whether the disperse phase is a solid or a liquid. As the dispersion is increased we obtain suspension and emulsion colloids which may be conveniently called *suspensoids* and *emulsoids*. Suspensoids and emulsoids are included under the general term *dispersoids*. In certain cases, although the disperse phase is unquestionably liquid, the systems resemble suspensoids in their behavior, while in other cases, where the disperse phase is solid, the systems exhibit properties characteristic of emulsoids. For this reason the classification of sols as suspensoids and emulsoids is not entirely satisfactory. A better system is that in which the presence or the absence of affinity between the disperse phase and the dispersion medium is made the basis of classification. Where there is marked affinity between the two phases, the system is termed *lyophile*, and where such affinity is absent, the system is termed *lyophobe*. When the dispersion medium is water, the terms *hydrophile* and *hydrophobe* are employed.

In the reversible transformation of a sol into a gel, we are not warranted in referring to the change from gel to sol as an act of solution, for if the gel really dissolved, a solution and not a sol would result. Various terms have been proposed for these reversible transformations but perhaps the most satisfactory are the terms *gelation* and *solation*, the former designating the formation of a gel from a sol and the latter the reverse process.

Lyotrope Series. The differences between lyophile and lyophobe sols are frequently very marked, this being especially true of their behavior toward chemical reagents. The action of chemical reagents on lyophobe sols is almost wholly confined to the disperse phase, while the addition of reagents to lyophile sols frequently produces a more marked effect on the dispersion medium than on the disperse phase. It should be observed that the physical properties of a lyophobe sol and of the pure dispersion medium are practically identical, while exactly the reverse is true of lyophile sols. It is well known that the addition of a foreign substance to a reaction-mixture frequently exerts a marked influence on the speed of the reaction, notwithstanding the fact that the nature of the added substance may be such as to render its participation in the reaction highly improbable. If a series of reagents are arranged in the order of their influence on a particular reaction, it has been found that the same sequence is preserved when the same reagents are added to other reactions of widely different character. In some reactions the reagents may produce effects directly opposite to those which they produce in others, but the sequence remains unchanged. For example, when the same reaction takes place either in an acid or in an alkaline medium, the substances which promote the reaction when the medium is acid, retard it when the medium is alkaline, but the sequence of the added substances remains the same under both conditions. These facts make it appear highly probable that the effects produced by the addition of foreign substances to a chemical reaction are to be ascribed to the changes which they produce in the pure solvent. It is not without significance that the same sequence of reagents is maintained whether we observe their influence on different chemical reactions or on certain physical properties of the solvent, such as its density, viscosity, and surface tension.

The following examples * afford a striking illustration of the persistence of the sequence of reagents, generally known as the *lyotrope series*. The ions which precede the formula (H_2O) reduce the velocity of reaction or cause a diminution in the magnitude of the particular physical property tabulated. The ions which follow the formula (H_2O) exert the opposite effect.

---

* Freundlich, Kapillarchemie, p. 411.

1. The hydrolysis of esters by acids.
   Anions: SO_4 (H_2O) Cl < Br.
   Cations: (H_2O) Li < Na < K < Rb < Cs.
2. The hydrolysis of esters by bases.
   Anions: I > NO_3 > Br > Cl (H_2O) S_2O_3 < SO_4.
   Cations: Cs > Rb > K > Li (H_2O).
3. The viscosity of aqueous solutions.
   Anions: NO_3 > Cl (H_2O) SO_4 (potassium salts).
   Cations: Cs > Rb > K (H_2O) Na < Li (chlorides).
4. The surface tension of aqueous solutions.
   (H_2O) I < NO_3 < Cl < SO_4 < CO_3.

It will be observed that although the ions which accelerate the acid hydrolysis retard the basic hydrolysis, the sequence of the ions nevertheless remains the same.

The Ultramicroscope. When a narrow beam of sunlight is admitted into a darkened room, the dust particles in its path are rendered visible by the scattering of the light at the surface of the particles. If the air of the room is free from dust, no shining particles will be seen and the space is said to be "optically void." When the particles of dust are very minute, the beam of light acquires a bluish tint. The blue color of the sky is thus attributed to the presence of extremely fine particles of dust in the air together with minute drops of condensed gases in the upper regions of the atmosphere.

The visibility of a beam of light due to the scattering effect of minute particles, is known as the *Tyndall phenomenon.* Almost all colloidal solutions exhibit this phenomenon when a powerful beam of light is passed through them, thus proving the presence of discrete particles in the solutions.

The ultramicroscope is an instrument devised by Siedentopf and Zsigmondy * for the detection of colloidal particles much too small to be seen by the naked eye. A powerful beam of light issuing from a horizontal slit is brought to a focus within the colloidal solution under examination by means of a microscope objective, and this image is viewed through a second microscope, the axis of which is at right angles to the path of the beam.

---

* "Colloids and the Ultramicroscope" by R. Zsigmondy. Trans. by Alexander. John Wiley & Sons, Inc.

When examined in this way a colloidal solution appears to be swarming with brilliantly colored particles, moving rapidly in a dark field; whereas a true solution, if properly prepared, appears optically void. With the ultramicroscope it is possible to count the number of particles present in a given volume of a colloidal solution. By means of a chemical analysis, the mass of colloid per unit of volume can be determined and from this the average mass of each particle can be calculated. If the particles be assumed to be spherical in shape and to have the same density as larger masses of the same substance, we can calculate the volume of a single particle and from this its diameter. Thus, Burton * in his experiments on gold, silver and platinum sols, found the average diameter of the colloidal particles to range from 0.2 to 0.6 micron.

Zsigmondy's latest ultramicroscope, Fig. 68, consisting of two compound microscopes placed at right angles and having their objectives so cut away as to permit them to be brought together in focus, enables the observer to discern particles whose diameters range from 1 to 2 milli-microns.

The ultramicroscopic character of emulsoids is by no means sharply defined, notwithstanding the fact that they exhibit the Tyndall phenomenon. It has been suggested by Zsigmondy that the lack of sharpness in definition observed with emulsoids is probably due to the relatively small difference between the refractive indices of the disperse phase and the dispersion medium. Where the difference between the refractive indices of the two phases is very great, as in the case of the metallic sols, excellent definition is obtained. It is of interest to note that although the basic hydroxides are apparently suspensoids, yet in their ultramicroscopic characteristics they closely resemble emulsoids.

Ultrafiltration. Almost all sols can be filtered through ordinary filter paper without undergoing more than a slight change in concentration due to initial adsorption. The rate of filtration varies widely, depending upon the viscosity of the sol. As a general rule, mulsoids filter more slowly than suspensoids owing to the high iscosity of the former.

---

* Phil. Mag., 11, 425 (1906).

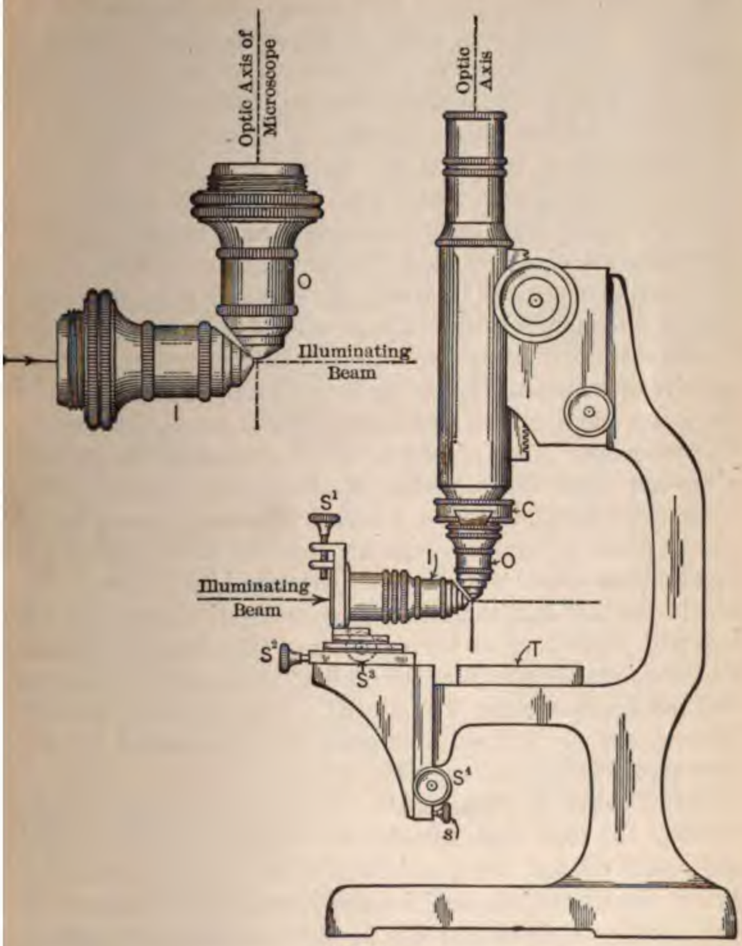


Fig. 68.

By filtering an arsenious sulphide sol through a porous earthenare filter, Linder and Picton * succeeded in obtaining four differ-

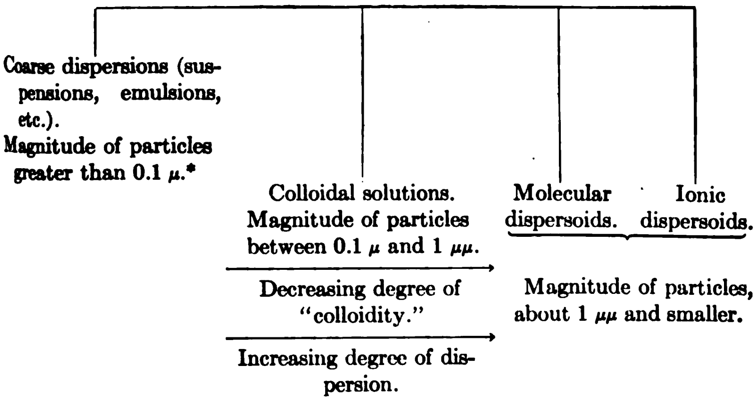
---

* Jour. Chem. Soc., **61**, 148 (1892).

ent sizes of particles which they described as follows: — (1) visible under the microscope, (2) exhibited the Tyndall phenomenon, (3) retained by porous plate, and (4) passed through porous plate unchanged. By employing plates of different degrees of porosity and determining the average size of the pores which just permit filtration, it is possible to determine the size of the particles which constitute the disperse phase of a sol. If we make use of a series of graduated filters, prepared by impregnating filter paper with a solution of collodion in acetic acid, it is not only possible to separate suspensoids from their dispersion media, but also to effect the concentration of emulsoids. Furthermore such filters are useful in removing impurities from sols, the impurity passing through the filter in a manner similar to the passage of the solvent through the membrane in the process of dialysis. Ultrafiltration is an exceedingly complex process involving the phenomena of adsorption and dialysis in addition to the ordinary process of mechanical separation. The complexity of the process is well illustrated by the phenomena attendant upon the filtration of almost any positive hydrosol. Thus, if we attempt to filter a ferric hydroxide hydrosol through a porous plate, or even through an ordinary filter paper, we shall find that the colloid will be partially retained by the filter. This is due to the fact that the filter becomes negatively charged in contact with water and, on the entrance of the positively charged sol into the pores of the filter, the colloid is immediately discharged and the disperse phase precipitated. After the pores of the filter become partially stopped with particles of the colloid, the sol will then pass through unchanged.

Classification of Dispersoids. There is abundant evidence in favor of the view that colloidal solutions and simple suspensions are closely related. Suspensions of all grades exist, from those in which the suspended particles are coarse-grained and visible to the naked eye, down to those in which a high-power microscope is required to render the suspended particles visible. Colloidal solutions have also been shown to be non-homogeneous, the presence of discrete particles being revealed by means of the ultramicroscope. It follows, therefore, that the size of the particles in solution determines whether a substance is to be considered as a colloid or not. At one extreme we have true solutions in which no lack of homogeneity can be detected, even by the ultramicroscope, and at the other extreme we have coarse-grained suspensions, in which the particles are visible to the naked eye. Between these two limits all possible degrees of subdivision are possible and it is a very difficult matter to draw sharp lines of distinction between true solutions and colloidal solutions on the one hand, and between colloidal solutions and suspensions on the other. One of the most satisfactory schemes of classification is that of von Weimarn and Wo. Ostwald.* Because of the fact that suspensions, colloidal solutions, and true solutions represent varying degrees of dispersion of the solute, all three types of system are termed by these authors, dispersoids. The dispersoids are classified as shown in the accompanying diagram.

DISPERSOIDS.



Coarse dispersions (suspensions, emulsions, etc.). Magnitude of particles greater than 0.1 μ.*

Colloidal solutions. Magnitude of particles between 0.1 μ and 1 $\mu\mu$.

Molecular dispersoids.

Ionic dispersoids.

Magnitude of particles, about 1 $\mu\mu$ and smaller.

$\xrightarrow{\hspace{3em}}$ Decreasing degree of "colloidity."

$\xrightarrow{\hspace{3em}}$ Increasing degree of dispersion.

* 1 μ = 1 micron = 0.001 mm.

Density of Colloidal Solutions. As we have seen, suspensoids are commonly regarded as sols in which the disperse phase is solid, while emulsoids are considered to be sols in which the disperse phase is liquid. While this distinction between the two classes of sols is generally well defined, it should be borne in mind that there are colloidal solutions in which it is extremely difficult to determine the physical state of the disperse phase.

---

* Koll. Zeitschrift, 3, 26 (1908).

The fundamental difference between suspensoids and emulsoids manifests itself most clearly in those properties which undergo appreciable change in consequence of solution. Among these may be mentioned density, viscosity and surface tension.

It was shown by Linder and Picton * that the density of suspensoids follows the law of mixtures. This is clearly shown by the following table in which are given the observed and calculated values of the density of a series of arsenious sulphide sols.

DENSITY OF ARSENIOUS SULPHIDE SOLS.

As_2S_3 (grams per liter).	Density (obs.).	Density (calc.).
44	1.033810	1.033810
22	1.016880	1.016905
11	1.008435	1.008440
2.45	1.002110	1.002100
0.1719	1.000137	1.000134

The density of emulsoids, on the other hand, cannot be calculated from the composition of the sol. This fact may be taken as evidence in favor of the view that a closer relation exists between the disperse phase and the dispersion medium in emulsoids than in suspensoids.

Viscosity of Colloidal Solutions. Owing to the fact that the concentrations of most suspensoids are relatively small, it follows that their viscosities differ but little from the viscosity of the pure dispersion medium. In general, it may be said that the viscosity of suspensoid sols is slightly greater than that of the dispersion medium.

On the other hand, the viscosity of emulsoid sols is frequently much greater than that of the pure dispersion medium. The viscosity of emulsoids also increases with increasing concentration, as is shown by the data of the following table.

---

* Jour. Chem. Soc., 67, 71 (1895).

VISCOSITY OF EMULSOIDS.

Sol.	Temp. 20° Concentration.	Viscosity.
	Per cent.	
Gelatine......	1	0.021
Gelatine......	2	0.037
Silicic acid....	0.81	0.012
Silicic acid...	0.99	0.016
Silicic acid...	1.96	0.032
Silicic acid....	3.67	0.165

Viscosity of water at 20° = 0.0120.

Surface Tension of Colloidal Solutions. The surface tension of suspensoid sols has been shown by Linder and Picton to be practically identical with that of the dispersion medium.

As a general rule, the surface tension of emulsoid sols is appreciably smaller than that of the dispersion medium. According to Quincke * the surface tensions of gelatine sols are appreciably less than the surface tension of the dispersion medium. The difference between suspensoids and emulsoids in respect to surface tension undoubtedly accounts for the fact that, in general, the former are not adsorbed while the latter are.

Osmotic Pressure of Colloidal Solutions. The osmotic pressure of colloidal solutions is very small. This is what we should expect with solutions of substances which exhibit a slow rate of diffusion. As has been pointed out, diffusion is closely connected with osmotic pressure; hence, if the rate of diffusion is slow, the osmotic pressure exerted by the solution should be small. In some cases the osmotic pressure is so small as to escape detection. The experimental determination of the osmotic pressure of colloidal solutions is complicated by the difficulty of removing the last traces of electrolytes from the colloid. Owing to their great osmotic activity, the presence of the merest trace of electrolytes may mask the true osmotic effect of the colloid. It should be borne in mind, however, that semipermeable membranes are much less permeable by colloids than by electrolytes and, in consequence of this fact, the impurities in the colloid would be gradually removed by prolonged dialysis. If the total osmotic pressure were due to the presence of small amounts of impurities in the colloid, then as these are removed, the pressure should steadily diminish and ultimately become zero. As a matter of fact, the final value of the osmotic pressure of a colloidal solution, although generally very small is never zero. This final, positive value of the osmotic pressure has been shown to be wholly independent of the method of preparation of the sol. Although differences in the method of preparation may introduce different impurities which give rise to different initial values of the osmotic pressure, in each case the same final value is obtained. Of course it must be admitted that the possibility exists that a minute portion of electrolyte which cannot be removed by dialysis is retained by the colloid, but even then it is difficult to account for the constancy of the final value of the osmotic pressure irrespective of the method of preparation of the sol. The values of the osmotic pressure of suspenoids are invariably small and by no means concordant.

---

* Wied. Ann., III, 35, 582 (1885).

The following table gives the results obtained by Duclaux* with colloidal solutions of ferric hydroxide.

OSMOTIC PRESSURE OF COLLOIDAL FERRIC HYDROXIDE.

Conc. $Fe(OH)_3$ Per cent.	Pressure in cm. of Water.
1.08	0.8
2.04	2.8
3.05	5.6
5.35	12.5
8.86	22.6

Inspection of the table shows that, even in the most concentrated solution, the osmotic pressure is very small. Furthermore, it is apparent that although the osmotic pressure increases with the concentration, the variables are not proportional. Observations on the variation of the osmotic pressure of colloidal solutions with temperature, show that, in general, as the temperature is raised the pressure increases at a more rapid rate than that required by the law of Gay-Lussac.

Employing membranes of collodion and parchment paper,

---

* Compt. rend., **140**, 1544 (1905); Jour. Chim. Phys., **7**, 405 (1909).

Lillie[*] and others have demonstrated that the values of the osmotic pressure of emulsoids are, in general, considerably greater than the corresponding values obtained with suspensoids. The osmotic pressures of several typical emulsoids are given in the following table.

OSMOTIC PRESSURES OF EMULSOIDS.

Sol.	Concentration (grams per liter).	Osmotic Pressure (mm. of mercury).
Egg albumin	12.5	20
Gelatine	12.5	6
Starch iodide	30	15
Dextrin	10	165

It will be observed that the values of the osmotic pressure in the preceding table are appreciably greater than those given for ferric hydroxide hydrosols. This is in agreement with the well-established fact that emulsoids diffuse more rapidly than suspensoids. It has been observed, that the value of the osmotic pressure of gelatine solutions at ordinary temperatures can be increased by maintaining the solutions at a higher temperature for a short time and then cooling to the initial temperature. After standing for several days at the original temperature, however, the osmotic pressure of the solution returns to its former value. This phenomenon would seem to indicate that the osmotic pressure of colloidal solutions is not completely defined by the two variables, temperature and concentration. It has been suggested that the degree of aggregation of the colloid is partially dependent upon the temperature; the molecular aggregates tending to break up as the temperature is raised, thus increasing the number of dissolved units and therefore causing a corresponding increase in the osmotic pressure.

Molecular Weight of Colloids. We have already learned that the knowledge of the osmotic pressure of a solution enables us to calculate the molecular weight of the solute, provided the solution is dilute and obeys the gas laws. As we have seen, other factors than concentration and temperature determine the osmotic pressure of colloidal solutions, so that we are not justified in attempting to calculate the molecular weight of a colloid from the observed value of the osmotic pressure of its solution. Values for the molecular weight of colloids calculated from their effect on the vapor pressure, the boiling-point, and the freezing-point of the solvent are also untrustworthy, since the same factors which influence the osmotic pressure necessarily affect these related properties. This becomes evident when we reflect that an osmotic pressure of 1 mm. of mercury corresponds to a depression of the freezing-point of about 0°.0001. Owing to the difficulty of obtaining absolutely pure emulsoid sols, all determinations of their freezing-point depressions must be affected with an experimental error appreciably larger than the observed depression. Hydrosols of albumin, gelatine, etc., prepared with extreme care by Bruni and Pappada * failed to produce any detectable depression of the freezing-point of water.

---

[*] Am. Jour. Physiol., **20**, 127 (1907).

Electroendosmosis. The movement of a liquid through a porous diaphragm, due to the passage of an electric current between two electrodes placed on opposite sides of the diaphragm, is known as *electroendosmosis*. This phenomenon, which was first observed by Reuss in 1807, has since been made the subject of numerous investigations by Wiedemann,† Quincke ‡ and Perrin,§ the latter having worked out a satisfactory theoretical interpretation of the phenomenon. If a porous partition be placed in the horizontal portion of a U-tube and an electrode be inserted in each arm of the tube, it will be found, on filling the tube with a feebly conducting liquid and passing a current, that the liquid will commence to rise in one arm of the tube and will continue to rise until a definite equilibrium is established. For a given difference of potential between the two electrodes, there will be a definite difference in the level of the liquid in the two arms of the tube. The majority of substances acquire a negative electric charge when

* Rend. R. Accad. dei Lincei, (5), **9**, 354 (1900).

† Pogg. Ann., **87**, 321 (1852).

‡ Ibid., **113**, 513 (1861).

§ Jour. Chim. Phys., **2**, 601 (1904).

immersed in water. The water, under these conditions, becomes positively charged and will, in consequence, migrate toward the cathode. On the other hand, certain substances acquire a positive charge on immersion in water and in these cases the direction of migration will obviously be reversed.

It has been found that acids cause negative diaphragms to become less negative and positive diaphragms to become more positive. The action of alkalies is, as we should expect, the reverse of that of acids. There is an interesting connection between the valence of the ions resulting from the dissociation of dissolved salts, and the difference of potential existing between the liquid and the diaphragm. When the diaphragm is positively charged, the difference of potential is found to be conditioned by the valence of the anion, and when the diaphragm is negatively charged, the difference of potential is determined by the valence of the cation.

Cataphoresis. When a difference of potential is established between two electrodes immersed in a suspension of finely-divided quartz or shellac, the suspended particles move toward the positive electrode. This phenomenon is called *cataphoresis* and was first observed by Linder and Picton.* They showed that when the terminals of an electric battery are connected to two platinum electrodes dipping into a colloidal solution of arsenious sulphide, there is a gradual migration of the colloid to the positive pole. A similar experiment with a solution of colloidal ferric hydroxide resulted in the transport of the dissolved colloid to the negative pole. It follows, therefore, that the particles of colloidal arsenious sulphide are negatively charged, while those of colloidal ferric hydroxide carry a positive charge. It has been found that all colloids carry an electric charge. In the table on page 252, some typical colloids are classified according to the character of their electrification in aqueous solution.

The nature of the charge varies with the dispersion medium used, colloidal solutions in turpentine, for example, having charges opposite to those in water.

Direct measurements of the velocity with which the particles move in cataphoresis have been made by Cotton and Mouton.* By observing with a microscope the distance over which a single particle traveled in a given interval of time under a definite potential gradient, they calculated the average velocity of migration of a number of suspensoids. The following table gives the velocity of migration of a few typical suspensoids.

---

* Jour. Chem. Soc., **61**, 148 (1892).

ELECTRICAL CHARGES OF HYDROSOLS.

Electro-positive.	Electro-negative.
Metallic hydroxides	All the metals
Methyl violet	Metallic sulphides
Methylene blue	Aniline blue
Magdala red	Indigo
Bismarck brown	Eosine
Hæmoglobin	Starch

VELOCITY OF MIGRATION OF SUSPENSOIDS.†

Suspensoid.	Average Diameter of Particles.	Velocity cm./sec. for Unit Potential Gradient.
Arsenic trisulphide	50 μ	22×10^{-5}
Quartz	1 $\mu\mu$	30×10^{-5}
Gold (colloidal)	<100 $\mu\mu$	40×10^{-6}
Platinum (colloidal)	<100 $\mu\mu$	30×10^{-5}
Silver (colloidal)	<100 $\mu\mu$	23.6×10^{-5}
Bismuth (colloidal)	<100 $\mu\mu$	11.0×10^{-5}
Lead (colloidal)	<100 $\mu\mu$	12.0×10^{-5}
Iron (colloidal)	<100 $\mu\mu$	19.0×10^{-5}
Ferric hydroxide (colloidal)	100 $\mu\mu$	30.0×10^{-4}

† Freundlich, Kapillarchemie, p. 234.

It will be observed that not only are the velocities of migration nearly constant, but also that they are apparently independent of the size and nature of the particles.

The presence of electrolytes, especially acids and bases, exercises a marked effect upon the electrical behavior of suspensoids. Owing to the comparative instability of suspensoids, the addition of electrolytes usually results in the complete precipitation of the colloid.

---

* Jour. Chim. Phys., 4, 365 (1906).

Emulsoids also show the phenomenon of cataphoresis, but their velocities of migration are appreciably less than the corresponding velocities of suspensoids, and their behavior in an electric field is such as to make it appear quite probable that the character of their electric charge is entirely fortuitous. Furthermore, emulsoids are much more susceptible to the influence of electrolytes than are suspensoids.

W. B. Hardy [*] has found that the direction of migration of albumin, modified by heating to 100° C., is dependent upon the reaction of the dispersion medium. A very small quantity of free base causes the particles of albumin to move toward the positive electrode, while the addition of an equally small amount of acid results in a reversal of the direction of migration. Similar reversals of charge have been observed by Burton [†] in colloidal solutions of gold and silver. When small amounts of aluminium sulphate are added to colloidal solutions of these metals, the charge is gradually neutralized and eventually the colloidal particles acquire a reversed charge.

Electrical Conductance of Colloidal Solutions. The electrical conductance of suspensoids differs so slightly from that of the pure dispersion medium that it is difficult to decide whether the small increase in conductance may not be due to the presence of traces of adsorbed electrolytes. In order to ascertain to what extent the conductance of suspensoids is dependent upon the presence of adsorbed electrolytes, Whitney and Blake [‡] investigated the effect of successive electrolyses upon the conductance of a gold hydrosol. If the pure sol is incapable of enhancing the conductance of the dispersion medium, then as the sol is subjected to successive electrolyses, the conductance should steadily diminish and ultimately become identical with that of the dispersion medium. Whitney and Blake found that the conductance converged to a definite limiting value which was slightly greater than the conductance of the dispersion medium. From these experiments we seem to be warranted in concluding that suspensoids conduct the electric current very feebly.

---

[*] Jour. Physiol., **24**, 288 (1899).

[†] Phil. Mag., **12**, 472 (1906).

[‡] Jour. Am. Chem. Soc., **26**, 1339 (1904).

Emulsoids appear to conduct rather better than suspensoids. Whitney and Blake measured the conductance of silicic acid and gelatine sols and found the specific conductance of the former to be 100×10^{-6} reciprocal ohms and that of the latter to be 68×10^{-6} reciprocal ohms. On the other hand, Pauli[*] found that an albumin sol which had been prepared with extreme care was virtually a non-conductor. It should be remembered, however, that the albumins are closely related to the simple amino-acids which are known to be exceedingly poor conductors.

Precipitation of Colloids by Electrolytes. One of the most important and interesting divisions of the chemistry of colloids is that which treats of the precipitation of suspensoids and emulsoids by electrolytes. In general, it may be said that the precipitation of colloids by electrolytes is an irreversible process. Colloidal solutions are more or less unstable systems irrespective of the methods employed in their preparation, and the addition of a small amount of an electrolyte is usually found to be sufficient to cause the sol immediately to become opalescent, and ultimately to precipitate, leaving the dispersion medium perfectly clear and free from the disperse phase. Some exceptions to this general statement as to the behavior of colloids are known. For example, Whitney and Blake[†] found that precipitated gold could be caused to return to the colloidal state by treatment with ammonia, while Linder and Picton[‡] discovered that a ferric hydroxide hydrosol, which had been precipitated with sodium chloride, could be restored to the colloidal condition by simply removing the electrolyte with water. The sedimentation of suspensions, such as kaolin in water, is also promoted by the addition of electrolytes.

On the other hand, non-electrolytes have no effect upon the stability of suspensoids or simple suspensions.

Precipitation of Suspensoids. The phenomenon of the precipitation of suspensoids has been carefully investigated by Freundlich.[§] He has found that an amount of electrolyte which is incapable of bringing about an instantaneous precipitation, may become effective after an interval of time. He has also shown that the total quantity of electrolyte required to precipitate a suspensoid completely depends upon whether the electrolyte is added all at one time or in successive portions. In order to compare the precipitating action of various electrolytes, Freundlich proposed the following procedure, which prevents the possibility of irregularities due to the time factor: — To 20 cc. of a solution of a suspensoid, 2 cc. of the solution of the electrolyte are added, the resulting solution being shaken vigorously; the mixture is then set aside for two hours, after which a small portion is filtered off, and the filtrate is examined for the suspensoid. In the following table some of the results obtained by Freundlich with colloidal solutions of ferric hydroxide are given. The data represent the minimum concentration for each electrolyte which produced precipitation in two hours.

---

[*] Beitrag. Chem. Phys. Path., **7**, 531 (1906).

[†] Jour. Am. Chem. Soc., **26**, 1341 (1904).

[‡] Jour. Chem. Soc., **61**, 114 (1892); **87**, 1924 (1905).

[§] Zeit. phys. Chem., **44**, 131 (1903).

It will be seen that very small amounts of the electrolytes are required to precipitate the suspensoid, and further, that the precipitating power of an electrolyte is dependent upon the charge of the negative ion. The greater the charge, the smaller is the quantity of electrolyte required to produce precipitation.

PRECIPITATING ACTION OF ELECTROLYTES ON FERRIC HYDROXIDE HYDROSOL.

(16 milli-mols $Fe(OH)_2$ per liter.)

Electrolyte.	Concentration (milli-mols per liter).
$NaCl$	9.25
KCl	9.03
$BaCl_2$	9.64
KNO_3	11.9
KBr	12.5
$Ba(NO_3)_2$	14.0
KI	16.2
HCl	400 ca.
$Ba(OH)_2$	0.42
$H_3(SO)_4$	0.204
$MgSO_4$	0.217
$K_2Cr_2O_7$	0.194
H_2SO_4	0.5 ca.

The significance of the relation between ionic charge and precipitating power was first pointed out by Hardy,[*] who formulated the following rule: — *The precipitation of a colloidal solution is determined by that ion of an added electrolyte which has an electric charge opposite in sign to that of the colloidal particles.*

It has already been pointed out that colloidal particles of arsenious sulphide are negatively charged, hence, according to Hardy's rule, the positive ions of the added electrolyte will condition the precipitation of the suspensoid. The experiments of Freundlich confirm this prediction, as is shown by the following table:

PRECIPITATING ACTION OF ELECTROLYTES ON ARSENIOUS SULPHIDE HYDROSOL.

(7.54 milli-mols As_2S_3 per liter.)

Electrolyte.	Concentration (milli-mols per liter).
KCl	49.5
KNO_3	50.0
$KC_2H_3O_2$	110.0
NaCl	51.0
LiCl	58.4
$MgCl_2$	0.717
$MgSO_4$	0.810
$CaCl_2$	0.649
$SrCl_2$	0.635
$BaCl_2$	0.691
$Ba(NO_3)_2$	0.687
$ZnCl_2$	0.685
$AlCl_3$	0.093
$Al(NO_3)_3$	0.095

Precipitation and Valence. An examination of the preceding tables reveals the fact that although the ionic concentration necessary to bring about precipitation, in accordance with Hardy's rule, decreases with increasing valence, the diminution in concentration is not, as we might expect, inversely proportional to the valence of the precipitating ion. The absence of any simple quantitative relation between the valence of an ion and its precipitating concentration is undoubtedly due to the influence of several potent factors, such as adsorption and the protective action of ions whose electric charge is of the same sign as that of the colloidal substance.

---

[*] Zeit. phys. Chem., 33, 385 (1900).

Precipitation of Emulsoids. The action of electrolytes on emulsoids is much more obscure than the action of electrolytes on suspensoids. Nothing approaching a generalization similar to Hardy's rule for the precipitation of suspensoids has been found to apply to the precipitation phenomena manifested by emulsoids. Owing to the fact that emulsoids are liquids, and in consequence of their greater degree of dispersity, it has been suggested that emulsoids probably resemble true solutions more closely than suspensoids. In fact there is reason for assuming that a portion of the colloid is actually dissolved in the dispersion medium. This may account for the fact that the precipitation of emulsoids is sometimes reversible and sometimes irreversible. It is to be regretted that, up to the present time, so many of the investigations on emulsoids have been carried out with materials of questionable purity and of insufficient uniformity.

The addition of salts to gelatine generally causes irreversible precipitation, provided the concentration of the salt is not too low.

The precipitation of albumin by some salts is reversible while by others it is irreversible. Those transformations which are initially reversible gradually become irreversible on standing. Although relatively concentrated solutions of salts of the alkalies and alkaline earths are required to precipitate albumin, very dilute solutions of the salts of the heavy metals are found to be sufficient to bring about complete precipitation.

Action of Heat on Emulsoids. When an albumin hydrosol is gradually heated, a temperature is ultimately reached at which coagulation occurs. The exact nature of this transformation is not understood, but it is believed to be largely chemical. This belief is based upon the fact that the reaction of the natural albumins toward litmus is altered by heating. Slight acidity of the sol is essential to complete coagulation, while an excess or a deficiency of acids causes a portion of the albumin to remain in the sol. The presence of various salts has been found to exert a marked influence on the temperature of coagulation of albumin.

The coagulation temperature is invariably raised at first, attainin a constant value in some cases, while in others it decreases afte reaching a maximum temperature. It is especially interesting t note that the anions of the salts follow the usual lytropic sequence

The effect of heat on a gelatine sol is very different from it effect on an albumin sol. If a fairly concentrated gelatine sol i heated and then permitted to cool, it sets into a jelly which is no reconverted into a sol when the temperature is again raised. Furthermore, the change does not take place at a definite temperature In studying the phenomenon of gelation, either the temperatur or the time of gelation may be determined. The melting-point o pure gelatine ranges from 26° to 29° while the solidifying temperature lies between 25° and 18°. The melting and solidifying temperature of gelatine sols vary with the concentration; a 5 per cen sol melts at 26°.1 and solidifies at 17°.8, while a 15 per cent so melts at 29°.4 and solidifies at 25°.5. The temperature of the gel sol transformation is affected by the addition of salts, some tendin to raise the temperature of gelation and others to lower it. Th order of the anions arranged according to their influence on th gel-sol transformation is as follows: —

Raising temperature: SO_4 > Citrate > Tartrate > Acetate (H_2O)
Lowering temperature: (H_2O) Cl < ClO_3 < NO_3 < Br < I.

The same lytropic order was found by Schroeder * in an investigation of the viscosity of gelatine sols.

It is noteworthy that the influence of salts on the temperatur of gelation of agar-agar and other similar substances is analogou to their effect on gelatine, the same lytropic sequence being maintained.

Protective Colloids. The precipitating action of electrolyte on suspensoids may be inhibited by adding to the solution of th suspensoid a reversible colloid. The protective action of a reversible colloid is not due, as might be supposed, to the increase viscosity of the medium and the resultant resistance to sedimentation, since amounts of a reversible colloid, too minute to produc any appreciable increase in the viscosity of the medium, can pre vent precipitation. Thus, Bechhold * has shown that while a mixture of 1 cc. of a suspension of mastic and 1 cc. of a 0.1 molar solution of $MgSO_4$ diluted to 3 cc. with water, is completely precipitated in 15 minutes, no precipitation will occur within 24 hours, if two drops of a 1 per cent solution of gelatine be added before diluting to 3 cc.

---

* Zeit. phys. Chem., 45, 75 (1903).

Gum arabic and ox-blood serum exert a similar protective action when added to a suspension of mastic. The protective power of reversible colloids differs widely and Zsigmondy † has attempted to make this the basis of a method of classification of colloidal substances. A red solution of colloidal gold becomes blue on the addition of a small amount of sodium chloride, owing to the increase in the size of the colloidal particles. Various colloidal substances when added to a red colored gold sol protect the colloidal particles from precipitation by a solution of sodium chloride, no change in color following the addition of the electrolyte. A definite amount of each colloidal substance is required to prevent the change from red to blue in the color of the gold sol. In employing this color change as a means of differentiating colloidal substances, Zsigmondy introduced the "gold number," which may be defined as the weight in milligrams of a colloidal substance which is just insufficient to prevent the change from red to blue in 10 cc. of a gold sol after the addition of 1 cc. of a 10 per cent solution of sodium chloride. The following table gives the gold numbers of a few colloids.

GOLD NUMBERS OF COLLOIDS.

Colloid.	Gold Number.
Gelatine	0.005–0.01
Casein (in ammonia)	0.01
Egg-albumin	0.15–0.25
Gum arabic	0.15–0.25; 0.5–4
Dextrin	6–12; 10–20
Starch, wheat	4–6 (about)
Starch, potato	25 (about)
Sodium stearate	10 (at 60°); 0.01 (at 100°)
Sodium oleate	0.4–1
Cane sugar	8
Urea	8

---

* Zeit. phys. Chem., **48**, 408 (1904).

† Zeit. analyt. Chem., **40**, 697 (1901).

The gold number has proven useful in differentiating the various kinds of albumin, as is shown in the following table.

GOLD NUMBERS OF ALBUMINS.

Albumin.	Gold Number.
Egg white (fresh).........	0.08
Globulin..................	0.02–0.05
Ovomucoid...............	0.04–0.08
Albumin (Merck).........	0.1–0.3
Albumin (cryst.)..........	2–8
Albumin (alkaline).......	0.006–0.04

The addition of alkali to any one of the first five albumins of the above table reduces the gold number to that of alkaline albumin. Sulphide sols may be protected as well as metallic sols, and furthermore the ability to exert protective action is not confined to organic colloids alone.

In general, it may be said that when a suspensoid sol is mixed with an emulsoid sol in the proper proportions, the suspensoid sol acquires most of the characteristic properties of the protecting colloid. The masking of the properties of a suspensoid sol by a protecting colloid is probably to be ascribed to the formation of a thin film of adsorbed emulsoid over the suspensoid.

Reciprocal Precipitation. A further deduction of the electrical theory of precipitation is, that when two oppositely-charged colloids are mixed, they should precipitate each other, and the resulting precipitate should contain both colloids. Experiments carried out by Biltz* have confirmed these predictions. He showed that when a solution of a positively-charged colloid is added to a solution of a negatively-charged colloid, precipitation occurs, unless the quantity of the added colloid is either relatively very large or very small. He also showed that when two colloids of the same electrical sign are mixed no precipitation occurs. Just as the amount of precipitation caused by the addition of an electrolyte to a sol is conditioned by the rate at which the electrolyte is added, so also the precipitation of one colloid by another is dependent upon the manner in which the two sols are mixed. The extent to which one sol is precipitated by another sol of opposite sign is largely determined by the amount of one that is added to a definite amount of the other. This is clearly shown by the data of the following table which give the results obtained by Biltz on adding ferric hydroxide sol to 2 cc. of an antimony trisulphide sol containing 2.8 mg. per cc.

---

* Berichte, 37, 1095 (1904).

PRECIPITATION OF COLLOIDAL ANTIMONY TRISULPHIDE BY COLLOIDAL FERRIC HYDROXIDE.

Fe_2O_3(mg.).	Immediate Result.	Result after One Hour.
0.8	Cloudy	Almost homogeneous
3.2	Small flakes	Unchanged
4.8	Flakes	Yellow liquid
6.4	Complete precipitation	Complete precipitation
8.0	Slow precipitation	Complete precipitation
12.8	Cloudy	Slight precipitation
20.8	Cloudy	Homogeneous

It will be seen that the addition of a small amount of ferric hydroxide produces hardly any precipitation. With the addition of larger amounts of ferric hydroxide, the amount of precipitation increases until finally complete precipitation is attained. The addition of larger quantities of ferric hydroxide produces either little or no precipitation. It has been found that at the concentration which just produces complete precipitation, the electrical charges on the two sols are equivalent. When the amount of ferric hydroxide exceeds that required for complete precipitation, it is more than probable that the particles of colloidal antimony trisulphide are completely enveloped by the particles of ferric hydroxide and thereby rendered inactive.

When we come to study the action of one emulsoid on another, we find, as might be expected from the general behavior of emulsoids toward electrolytes, that the phenomena are more complex and very much less well-defined than with suspensoids. Although mutual precipitation does take place with emulsoids, the close resemblance between emulsoids and true solutions renders the phenomenon more or less indistinct.

When a suspensoid sol is added to an emulsoid sol having an opposite electric charge, precipitation may or may not occur according to the relative amounts of the two colloids in the mixture. When the two colloids are present in electrically equivalent quantities precipitation occurs, otherwise one colloid exerts a protective action on the other.

Characteristics of Gels. Gels are generally obtained by cooling or evaporating emulsoid sols and, since the latter are known to be two-phase liquid systems, it is natural to infer that gels may also be two-phase systems. According to this conception, the only difference between an emulsoid sol and a gel is, that in the latter the concentration of at least one of the phases is greatly increased and thereby imparts greater viscosity and rigidity to the system. It has been suggested that the more concentrated of the two phases forms the walls of an assemblage of cells within which the more dilute phase is enclosed. The view that gels possess a distinct cellular structure is fully confirmed by microscopic examination.

The extreme sensitiveness of gels to changes in temperature and to the presence of extraneous substances renders their investigation exceedingly difficult. Notwithstanding the experimental difficulties involved in the study of gels, sufficient knowledge has been gained of their properties to make a brief account of these necessary in any treatment of the subject of colloids.

Physical Properties of Gels. The process of gel formation from a dry gelatinous colloid and water invariably involves contraction. This statement should not be confused with the fact that a gel on immersion in water undergoes appreciable increase in volume.

Gels have been shown by Barus * to be considerably more compressible than solids. The compressibility increases as the temperature is raised until, when the gel is transformed into the sol, the compressibility becomes equal to that of pure water. The temperature of some gels, such as rubber and gelatine, is lowered by compression and raised by tension.

The thermal expansion of gels is nearly identical with that of the more fluid component of the gel.

---

* Am. Jour. Sci., **6**, 285 (1898).

The rate at which pure substances diffuse in gels differs only slightly from the rate of diffusion in pure water, provided the concentration of the gel is not too great. The slight resistance offered by gels to diffusion of dissolved substances may be regarded as further evidence in favor of their cellular structure.

The modulus of elasticity of a gel, cast in a cylindrical mold, is given by the formula

$$E_d = \frac{Pl}{\pi r^2 \Delta l},$$

where P is the tension which produces the increase in length Δl in a cylinder whose length is l and whose radius is r. It has been found that the modulus of elasticity in gelatine gels increases as the square of the concentration of the gel. The time of recovery, after releasing the tension, increases as the concentration of the gel increases.

The shearing modulus for a gel is given by the formula

$$E_s = \frac{E_d}{2\,(1 + \mu)},$$

where μ denotes the ratio of the relative contraction of the diameter to the relative change in length. The viscosity of a gel may be calculated from the shearing modulus by means of the equation

$$\eta = E_s \tau,$$

where τ denotes the time of recovery. Since both E_s and τ increase with the concentration of the gel it is apparent that the viscosity of the gel must also increase with the concentration.

As is well known, when glass is subjected to pressure or is unequally strained, it exhibits the phenomenon of double refraction. Since glass bears some resemblance to gels in being a highly viscous, supercooled liquid, it might reasonably be inferred that gels should also show double refraction. Experiments with collodion and gelatine have shown that these substances, when subjected to pressure, behave similarly to glass.

Hydration and Dehydration of Gels. The complementary processes of hydration and dehydration of gels are extremely interesting. Following Freundlich * we will consider the subject very briefly under the two following heads: (a) Non-elastic Gels and (b) Elastic Gels.

(*a*) *Non-elastic Gels.* When freshly prepared aluminium or ferric hydroxide gels were placed in a desiccator, it was found by van Bemmelen † that the rate at which these substances lost water was continuous. Furthermore, on removing the dried gels from the desiccator it was found that the process of recovery of moisture was also continuous. It will be shown in a subsequent chapter (p. 320) that a definite hydrate in the presence of its products of dissociation, possesses a constant vapor pressure so long as any of that particular hydrate is present. The fact that the vapor pressure of the gels investigated by van Bemmelen did not remain constant but decreased continuously as the water was removed, proved conclusively that no chemical compounds were formed in the process of gel hydration.

Another gel which has been made the subject of much careful investigation is silicic acid. The dehydration curve of silicic acid is continuous, with the exception of a short portion where an appreciable amount of water is lost without much of any change in the vapor pressure. This portion of the curve corresponds to a marked change in the appearance of the gel. The gel which had hitherto been clear and transparent became opalescent soon after the vapor pressure had attained a temporarily constant value. The opalescence gradually permeated the entire mass, until the gel acquired a yellow color by transmitted light, and a bluish color by reflected light. These colors suggest a marked increase in the degree of dispersity of the gel, an inference the correctness of which subsequent investigation has fully confirmed.

The curve of hydration, while resembling the curve of dehydration in many respects, departs quite widely from it in others. The change in dispersity, as indicated by the appearance in reverse order of the color and opalescent phenomena mentioned above, also was manifest.

---

* Kapillarchemie, p. 486.

† Zeit. anorg. Chemie, **5**, 466 (1894); **13**, 233 (1897); **18**, 14, 98 (1898); **30**, 265 (1902).

(*b*) *Elastic Gels.* The absence in elastic gels of a horizontal portion in the dehydration curves, and the fact that although elastic gels may have become saturated with water vapor, they still retain the power of taking up large amounts of liquid water when immersed in that medium, constitute the chief differences between elastic and non-elastic gels.

The amount of water which can be taken up by an elastic gel is exceedingly large. Thus, on exposing a plate of gelatine weighing 0.904 gram for eight days in an atmosphere saturated with water vapor, Schroeder * found that it had taken up 0.37 gram of water. On exposing for a longer period of time under the same conditions, he found no further gain in weight, and on removing the gelatine plate from the moist atmosphere and placing it in a desiccator, the plate slowly gave up the absorbed moisture and regained its original weight. On the other hand, when the plate, after having absorbed the maximum weight of moisture from the air, was immersed in water, it was found to increase in weight very rapidly. Thus, on immersing the above plate which weighed 1.274 grams when saturated in moist air, and allowing it to remain in water for one hour, it was found to have taken up 5.63 grams of water. After an immersion of twenty-four hours, the plate was found to have taken up the maximum weight of water it was capable of absorbing at that temperature. On removing the plate, it was found to part with the absorbed water very readily, even in moist air, the greater part of the absorbed water being so loosely held that the vapor pressure of the gel remained the same as that of pure water at the temperature of the experiment.

It is impossible to measure directly the pressure produced by gels when they take up water, but some idea of the magnitude of these pressures may be obtained by coating a glass plate with gelatine, which has imbibed the maximum amount of water, and observing the degree to which the glass plate is bent by the drying gelatine film. Frequently the elastic limit of the glass is exceeded and the plate breaks under the stress produced by the dehydration of the gel.

---

* Zeit. phys. Chem., **45**, 75 (1903).

Velocity of Imbibition. The rate at which gels imbibe water has been studied by Hofmeister.* The velocity of imbibition of water by thin plates of gelatine and agar-agar was measured by removing the plates at definite intervals and determining their increase in weight. Owing to the time consumed in making the weighings, the time intervals are affected by an appreciable error. The following table gives the data of a single experiment with gelatine.

VELOCITY OF IMBIBITION IN GELATINE.
(Thickness of plate 0.5 mm.)

Time (min.).	Water Imbibed (grams).	k
5	3.08	0.090
10	3.88	0.084
15	4.26	0.084
20	4.58	0.064
25	4.67	0.075
∞	4.96	....

If the weight of water imbibed in t minutes is w_t, and w_∞ is the maximum weight of water which a gel can take up under the conditions, then the velocity of imbibition should be given by the equation

$$\frac{dw}{dt} = k\,(w_\infty - w_t),$$

which on integration becomes

$$k = \frac{1}{t}\log_e \frac{w_\infty}{(w_\infty - w_t)}\cdot$$

The figures in the third column of the preceding table were calculated by means of this equation and, although the values are not strictly constant, the variation is no greater than might be expected where the experimental error is so large.

Heat of Imbibition. The process of imbibition is accompanied by an evolution of heat. Quantitative measurements of the heat evolved when gels take up water have been made by Wiedemann and Lüdeking * and also by Rodewald.† The following table gives Rodewald's data on the heat of imbibition of starch.

---

* Arch. exp. Pathol. u. Pharmakol., 27, 395 (1890).

HEAT OF IMBIBITION OF STARCH.
(Weight of dry starch 100 grams.)

Per Cent, Water.	Heat in Calories per Gram of Starch.
0.23	28.11
2.39	22.60
6.27	15.17
11.65	8.43
15.68	5.21
19.52	2.91

It will be observed that the greatest development of heat accompanies the initial stages of imbibition where very small amounts of water are taken up. This is what we might expect when we remember that it is the last remaining portion of water which is most difficult to remove from a gel, and that it is only through the application of heat that its complete removal can be effected.

Imbibition in Solutions. When a gel is immersed in a saline solution, the salt distributes itself between the solvent and the gel. The rate of imbibition is found to vary greatly according to the salt which is present in the solution. Thus, the velocity of imbibition has been found to be accelerated by the presence of the chlorides of ammonium, sodium and potassium and by the nitrate and bromide of sodium; on the other hand, the presence of the nitrate, sulphate and tartrate of sodium retard imbibition.

The effect of acids and bases on imbibition appears to be similar to the influence of salts.

Adsorption. The change in concentration which occurs at the boundary between two heterogeneous phases is termed *adsorp-*

---

* Wied. Ann., **25**, 145 (1885).

† Zeit. phys. Chem., **24**, 206 (1897).

tion. At the surface of a solid surrounded by a gas or vapor, the phenomenon is generally known as gaseous adsorption, since any difference which may occur in the concentration of the solid phase is much too small to be detected. At the boundary between liquid and gaseous phases, the concentration of each phase undoubtedly undergoes alteration. In the case of the boundary between solid and liquid phases, the only apparent inequality in concentration occurs on the liquid side of the boundary, notwithstanding the fact that the adsorbed substance is quite commonly regarded as being bound to the surface of the solid phase. The cause of this erroneous conception is, that the extremely thin layer of liquid in which the alteration in concentration actually occurs, is the layer which wets the surface of the solid and hence is the layer which adheres to the solid when it is removed from the liquid.

The retention of gases by charcoal is a typical example of gaseous adsorption, while the removal of coloring matter by charcoal in the purification of various organic substances may be cited as an example of adsorption of a liquid by a solid.

If the adsorbed substance increases in concentration in the vicinity of the boundary, the adsorption is said to be *positive;* if it decreases, the adsorption is said to be *negative.*

Adsorption of Gases. In gases, adsorption-equilibrium is attained with remarkable rapidity. Thus, if a gas is admitted into a vessel containing some freshly prepared cocoanut charcoal, the pressure will fall immediately to a value which corresponds to the removal of the entire adsorbed volume of gas.

The concentration of adsorbed gas on the surface of a solid, when equilibrium is attained, has been shown to be approximately 1×10^{-7} gram per square centimeter. This value is of the same order of magnitude as the strength of the limiting capillary layer of a liquid and, therefore, lends support to the suggestion put forward some years ago by Faraday that an adsorbed film of gas may be present in the liquid state.

The amount of gas adsorbed by a solid increases with the pressure and diminishes with increasing temperature. The following empirical equation, expressing the relation between the amount of gas adsorbed by a solid and the pressure, has been proposed by Freundlich *

$$\frac{x}{m} = \alpha p^{\frac{1}{n}},$$

where x is the total mass of gas adsorbed on a surface of m sq. cm. under a pressure p, and where α and n are constants. This equation, known as the *adsorption isotherm*, has been found to hold quite generally.

Adsorption in Solutions. The adsorption phenomena occurring at the surface of contact of a solid with a solution are similar to the phenomena which have just been discussed. Because of the frequency of its occurrence in many of the more common operations of both laboratory and factory, the subject of adsorption in solutions deserves fuller treatment.

The general characteristics of adsorption in solutions may be briefly summarized as follows: —

(1) Adsorption in solutions is generally positive, *i.e.*, on shaking a solution with a finely-divided adsorbent, the volume concentration of the solution will diminish.

(2) The amount of positive adsorption may be sufficient to remove almost all of the solute from a solution, especially if the solution is dilute. On the other hand, negative adsorption is always very small, and frequently is immeasurable.

(3) Adsorption is directly proportional to the so-called "specific surface," the latter term being defined as the ratio of the total surface of the adsorbent to its volume.

(4) On shaking a definite weight of an adsorbent with a given volume of solution of known concentration, a definite equilibrium will be established. If the solution is then diluted with a known amount of solvent, the adsorption will decrease until it acquires the same value which it would have attained, had the same weight of adsorbent been introduced directly into the more dilute solution. For example, if 1 gram of charcoal is agitated with 100 cc. of a 0.0688 molar solution of acetic acid for 20 hours, adsorption is found to reduce the original concentration of the acid to 0.0678 molar.

---

* Zeit. phys. Chem., 57, 385 (1906).

In a second experiment, if 1 gram of charcoal is shaken for the same period of time with 50 cc. of $2 \times 0.0688 = 0.1376$ molar acetic acid, and then, after adding 50 cc. of water, the shaking is continued for an additional period of 3 hours, the final concentration of the acid will be found to be the same as in the first experiment.

(5) It is impossible to determine the specific surface of an adsorbent directly owing to its porosity. However, according to (3) adsorption is directly proportional to the specific surface and therefore the weights of different adsorbents which produce the same amount of adsorption may be assumed to possess equal specific surfaces.

(6) Adsorption in solution is largely dependent upon the surface tension of the solvent. In solutions of the same substance in different solvents, the greatest adsorption occurs in that solution whose solvent possesses the highest surface tension.

(7) The order of efficiency of adsorption is not only independent of the nature of the solvent but also of the nature of the adsorbed substance.

The Adsorption Isotherm. The empirical equation of Freundlich for gaseous adsorption has been found to apply equally well to adsorption equilibria in solutions. The equation may be written as follows:

$$\frac{x}{m} = \alpha c^{\frac{1}{n}},$$

where x is the weight of substance adsorbed by a weight m of adsorbent from a solution whose volume-concentration at equilibrium is c, and where, as before, α and n are constants. The constant n varies in different cases from $n = 2$ to $n = 10$; within these limits the value of n is independent of the temperature and also of the natures of the adsorbed substances and the adsorbent. Although the value of the constant α varies over a wide range, the ratio of its values for two adsorbents in different solutions is practically constant.

The following table contains the data given by Freundlich[*] on the adsorption of acetic acid by charcoal.

---

[*] Kapillarchemie, p. 147.

ADSORPTION OF AQUEOUS ACETIC ACID BY CHARCOAL.

$t = 25°$; $\alpha = 2.606$; $1/n = 0.425$.

Concentration (mols per liter).	x/m (obs.).	x/m (calc.).
0.0181	0.467	0.474
0.0309	0.624	0.596
0.0616	0.801	0.798
0.1259	1.11	1.08
0.2677	1.55	1.49
0.4711	2.04	1.89
0.8817	2.48	2.47
2.785	3.76	4.01

The validity of the adsorption isotherm is best tested graphically, by plotting the logarithms of the experimentally determined values of x/m against the logarithms of the corresponding concentrations. If the equation holds, a straight line should be obtained. The curves shown in Fig. 69 represent x/m as a function of c, and $\log x/m$ as a function of $\log c$: it will be observed that the logarithmic plot is practically rectilinear.

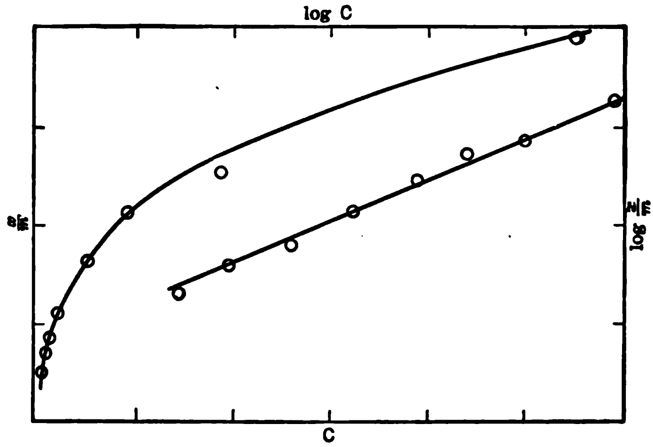


Fig. 69.

Surface Energy of Colloids. In almost all colloidal solutions there exists a difference of potential between the particles of the colloid and the surrounding medium. The importance of this factor in interpreting the behavior of colloids has already been emphasized. Another factor of equal importance in connection with colloidal phenomena, is that which depends upon the enormous surface of contact between the colloid and the surrounding medium. There is an abundance of evidence showing that a colloidal solution is non-homogeneous, or in other words, that it is essentially a suspension of finely-divided particles in a fluid medium. An immense increase in superficial area results from the division and subdivision of matter. To bring about this comminution requires a large expenditure of energy. In a colloidal solution this energy is stored up in the colloidal particles in the form of surface energy, which may be defined as the product of surface area and surface tension.

For example, suppose 1 cc. of a substance to be reduced to cubical particles measuring 0.1 μ on each edge, and let the particles be suspended in water at 17° C. The total energy involved can be calculated as follows: — The volume of a single particle is $0.1\ \mu^3$ or 1×10^{-15} cc.; hence the total number of particles is 1×10^{15}. The surface of a single particle is $6 \times (0.1\ \mu)^2$, or 6×10^{-10} sq. cm., and the total surface is 6×10^5 sq. cm. The surface tension of water at 17° C. is 71 dynes; hence the total surface energy is $71 \times 6 \times 10^5 = 4.32 \times 10^7$ ergs. This enormous figure shows that where the surface of the disperse phase is highly developed, as it is in colloidal solutions, the surface energy becomes a very important factor in determining the behavior of the system. This is especially the case when the degree of aggregation of the colloidal particles is changed, since a relatively small change in the amount of aggregation may involve a great change in the surface exposed and a corresponding change in the surface energy. A very close connection exists between the electrical and surface factors in a colloidal solution.

Surface Concentration. It has been pointed out in an earlier chapter (p. 144) that as the result of unbalanced molecular attraction, the surface of a liquid behaves like a tightly stretched membrane. In consequence of this contractile force, or surface tension, the pressure at the surface of a liquid is greater than the pressure within the liquid.

The experiments of Soret (p. 208) and the theoretical deductions of van't Hoff have shown that when a dilute solution is unequally heated, the solute distributes itself in accordance with the gas laws, the solution becoming more concentrated in the cooler portion. Just as the homogeneity of a dilute solution has been shown to be disturbed by inequality of temperature, so also inequality of pressure may be assumed to cause differences in concentration in the solution. Although direct experimental verification is difficult, there is abundant evidence for the view that the concentration at the surface of solution differs from the volume-concentration of the solution in consequence of the greater pressure in the surface layer.

The mathematical relation between surface concentration and surface tension was first deduced by J. Willard Gibbs * in 1876. The following simplified derivation of this important equation is due to Ostwald. Let s be the surface of a solution whose surface tension is γ, and let it be assumed that the surface contains 1 mol of the solute. If a very small portion of the solute enters the surface layer from the solution, thereby causing a diminution $d\gamma$ in the surface tension, the corresponding change in energy will be $s\,d\gamma$. But this gain in energy must be equivalent to the osmotic work involved in effecting the removal of the same weight of solute from the solution. Let v be the volume of solution containing unit weight of solute, and let dp be the difference in the osmotic pressures of the solution before and after its removal: the osmotic work will be $-v\,dp$. Since the gain in surface energy and the osmotic work are equal, we have

$$s\,d\gamma = -v\,dp.$$

The solutions being dilute, we may assume that the gas laws hold, and since $v = RT/p$, we may write

$$s\,d\gamma = -\frac{RT}{p}\,dp,$$

or

$$\frac{d\gamma}{dp} = -\frac{RT}{sp}.$$

---

* Trans. Conn. Acad., Vol. III, 439 (1876).

Since pressure is directly proportional to concentration, the preceding equation becomes

$$\frac{d\gamma}{dc} = -\frac{RT}{sc}.$$

But s has already been defined as the surface which contains 1 mol of solute in excess, from which it follows that the excess of solute in unit surface is $1/s$. Writing $u = 1/s$, we have

$$u = -\frac{c}{RT}\frac{d\gamma}{dc},$$

which is the equation of Gibbs.

From this equation it is evident that if the surface tension, γ, increases with the concentration, then u is negative and the surface concentration is less than the concentration of the bulk of the solution. This is clearly negative adsorption. On the other hand, if γ decreases as the concentration increases, u is positive and the surface concentration is greater than the concentration of the bulk of the solution, or the adsorption is positive. Finally, if the surface tension is independent of the concentration, then the concentration of the solute in both the surface layer and the bulk of the solution will be the same.

Preparation of Colloidal Solutions. Since 1861, when Graham published his first paper on colloids, numerous investigators have devised methods for the preparation of colloidal solutions. Within recent years our knowledge of this class of solutions has been greatly increased, many crystalloidal substances having been obtained in the colloidal condition. As a result of these investigations, we no longer speak of crystalloidal and colloidal matter, but use the terms crystalloid and colloid to distinguish two different states. In fact it is now recognized that it is simply a matter of overcoming certain experimental difficulties, before it will be possible to obtain all forms of matter in the colloidal state. The scope of this book forbids a detailed account of the various methods which have been devised for the preparation of colloidal solutions.* We must content ourselves with a general classification of these methods into two groups as follows: —

---

* See "Die Methoden zur Herstellung Kolloider Lösungen anorganischer Stoffe," by Theodore Svedberg, Dresden, 1909.

(1) Crystallization Methods, and (2) Solution Methods. These two divisions are sufficiently comprehensive to include all of the known methods for the preparation of colloidal solutions, with the possible exception of the electrical methods which may be considered as forming a separate group.

Crystallization Methods. The crystallization methods include the following subdivisions: —

(1) *Methods involving cooling of a liquid or solution.*

Example: — On cooling an alcoholic solution of sulphur in liquid air, a transparent, highly dispersed, solid sol is obtained.

(2) *Methods involving change of medium.*

Example: — On gradually adding a solution of mastic in alcohol to a large volume of water, the mastic is precipitated in a finely divided condition and a colloidal mastic hydrosol results.

(3) *Reduction methods.*

Example: — On adding a cold, dilute solution of hydrazine hydrate to a dilute, neutral solution of auric chloride, a dark blue gold sol is obtained.

In addition to hydrazine, numerous other reducing agents may be employed, such as phosphorus, carbon monoxide, hydrogen, acetylene, formaldehyde, acrolein, various carbohydrates, hydroxylamine, phenylhydrazine, and metallic ions.

(4) *Oxidation methods.*

Example: — On oxidizing a solution of hydrogen sulphide by air or sulphur dioxide, a colloidal solution of sulphur is obtained.

(5) *Hydrolysis methods.*

Example: — When a solution of ferric chloride is slowly added to a large volume of boiling water, the salt undergoes hydrolysis, and on cooling the dilute solution, a reddish-brown ferric hydroxide sol is obtained.

(6) *Methods involving metathesis.*

Example: — A colloidal solution of silver may be prepared by adding a few drops of a dilute solution of sodium chloride to a dilute solution of silver nitrate, provided the resulting solution of sodium nitrate is below the precipitating concentration.

Solution Methods. Under this heading are to be grouped so-called "*peptization*" methods. The term, peptization, was i duced by Graham to express the transformation of a gel into To-day we understand a peptizer to be a substance whic sufficiently concentrated, is capable of effecting the solution solid which is insoluble in its dispersion medium. A ty example of peptization is afforded by silver chloride which for sol on prolonged digestion with a solution which contains ei $Ag^{\cdot}$ or Cl'. It is apparent that the rate of peptization can be trolled by dilution of the peptizer, and that when the sol sta attained, the peptizer may be readily removed by dialysis.

Numerous reactions are known in which the conversion o insoluble precipitate into a sol can only be effected through removal of the excess of electrolyte by prolonged washing or ysis. A familiar example of this type of peptization is furni by the tendency of many precipitates to run through the f after too prolonged washing with water.

Electrical Methods. These methods of preparing colloidal s tions depend upon the dispersive action of a powerful ele discharge upon compact metals. In 1897 Bredig[*] discove while studying the action of the electric current on diffe liquids, that if an arc be established between two metallic w immersed in a liquid, minute particles of metal are torn off f the negative terminal and remain suspended in the liquid in nitely. In order to prepare a colloidal solution by the metho electrical dispersion, Bredig recommends that a direct cur arc be established between wires of the metal of which a collo solution is desired, the ends of the wires being submerged in w in a well-cooled vessel, as shown in Fig. 70. The current emplo ranges in strength from 5 to 10 amperes, and the voltage lies tween 30 and 110 volts. A rheostat and an ammeter are inclu in the circuit.

The wires are brought in contact for an instant in orde establish the arc, after which they are separated about 2 During the gentle hissing of the arc, clouds of colloidal metal projected out into the water from the negative wire, a portion the metal torn off being distributed through the water as a coarse suspension. The size of the particles disrupted from the negative terminal is dependent upon the strength of the current, a current of 10 amperes producing a greater proportion of colloidal metal than a current of 5 amperes. The addition of a trace of potassium hydroxide to the water has been shown to facilitate the process of dispersion. When gold wires are used, deep red colloidal solutions are obtained, which after standing for several weeks, acquire a bluish-violet color. With extra precautions, the red colloidal gold solutions may be preserved for two years. These solutions have been shown by Bredig to contain about 14 mg. of gold per 100 cc. In this manner Bredig prepared colloidal solutions of platinum, palladium, iridium, and silver. The method of Bredig has been improved and extended by Svedberg.

---

[*] Zeit. Elektrochem., 4, 514 (1897); Zeit. phys. Chem., 31, 258 (1899)

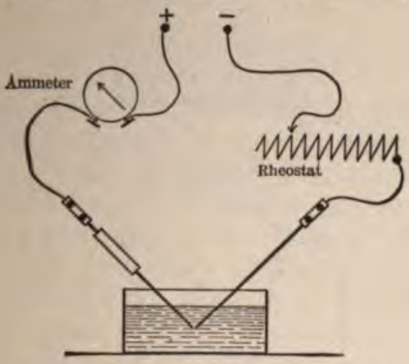


Fig. 70.

A diagram of Svedberg's apparatus is shown in Fig. 71. The secondary terminals of an induction coil, capable of giving a spark ranging from 12 to 15 cm. in length, are connected in parallel with the electrodes and a glass plate-condenser having a surface of approximately 225 sq. cm. Minute fragments or grains of the metal of which a sol is desired are placed on the bottom of the vessel containing the dispersion medium. The electrodes, which need not necessarily be of the same metal, are immersed as shown in the diagram, and during the process of electrical dispersion, the contents of the vessel are gently stirred with one or the other of the electrodes. With this apparatus Svedberg has succeeded in preparing colloidal solutions of tin, gold, silver, copper, lead, zinc, cadmium, carbon, silicon, selenium, and tellurium. He has also obtained all of the alkali metals in the colloidal state, ethyl ether being used as the dispersion medium. An interesting observation made by Svedberg in the course of his experiments is that the color of a metal is the same in both the colloidal and gaseous states.

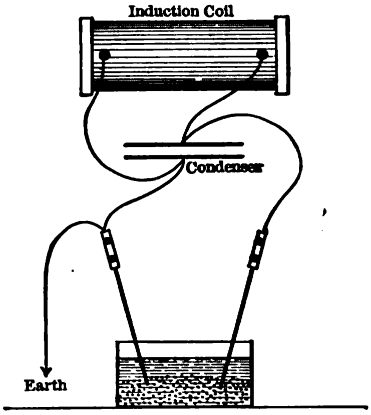


Fig. 71.

CHAPTER XIII.

MOLECULAR REALITY.

The Brownian Movement. If a liquid in which fine particles of matter are suspended, such as an aqueous suspension of gamboge, be examined under the microscope, the suspended particles will be seen to be in a state of ceaseless, erratic motion. This phenomenon was first observed in 1827 by the English botanist, Robert Brown, while examining a suspension of pollen grains, and has been called the *Brownian Movement* in honor of its discoverer.

Ever since its discovery, the Brownian Movement has been the subject of numerous investigations. It was not until 1863, however, that Wiener suggested that the cause of the phenomenon was the actual bombardment of the suspended particles by the molecules of the suspending medium. Twenty-five years later a similar conclusion was reached independently by Gouy, who showed that neither light nor convection currents within the liquid could possibly give rise to the motion. Furthermore, Gouy showed the movement to be independent of external vibration and only slightly influenced by the nature of the suspended particles. The smaller the particles and the less viscous the suspending medium, the more rapid the motion was found to be. By far the most striking feature of the phenomenon, however, is the fact that the motion is ceaseless.

Perrin's Experiments. The first quantitative investigation of the Brownian Movement was undertaken by Perrin in 1909. It has been shown (p. 100) that the mean kinetic energy E_k of one mol of a perfect gas is given by the expression

$$E_k = \tfrac{3}{2}\, pv. \tag{1}$$

Since $pv = RT$, we may write

$$E_k = \tfrac{3}{2}\,\frac{RT}{N}, \tag{2}$$

where N denotes the Avogadro Constant, *i.e.*, the number molecules contained in one mol of any gas. It is evident that E_k can be measured, equation (2) affords a means of calculating provided we are warranted in applying an equation which has bee derived for the gaseous state to a suspension of fine particles in liquid medium. It has already been shown that the simple ga laws hold for dilute solutions and therefore we may assume tha at the same temperature, the mean kinetic energy of the dissolve molecules is equal to that of the gaseous molecules. In oth words, at the same temperature, the mean kinetic energy of the molecules of all fluids is the same, and is directly proportion to the absolute temperature. Since the gas laws apply equa well to dilute solutions containing either large or small molecul Perrin held that there was no *a priori* reason for assuming that t grains of a suspension should not conform to the same laws. this assumption be correct, the grains of a uniform suspens should so distribute themselves under the influence of grav that, when equilibrium is attained, the lower layers will have higher concentration than the upper layers. In other words, t distribution should be strictly analogous to the distribution of t air over the surface of the earth, the density being greatest at t surface and diminishing as the altitude increases.

Let us imagine a suspension to be confined within a t vertical cylinder whose cross-sectional area is s sq. cm. A suming that the suspension has come to equilibrium under t influence of gravitation, let n be the number of grains per unit volume at a height h from the base of the cylinder. Since t concentration diminishes as the height increases, the number grains at a height $h + dh$ will be $n - dn$. The osmotic pressu of the grains at the height h will be $\frac{2}{3}\,nE_k$, where E_k is the me kinetic energy of each grain. In like manner, the osmotic pressu at the height $h + dh$ will be $\frac{2}{3}\,(n - dn)\,E_k$. The difference osmotic pressure between the two levels is $-\frac{2}{3}\,dnE_k$ and since t pressure acts over a surface of s sq. cm., the difference of osmot forces acting over the cross-sectional area of the cylinder $-\frac{2}{3}\,s\,dnE_k$. Since the system is in equilibrium, this difference osmotic forces must be balanced by the difference in the attractic of gravitation at the two levels. Let ϕ be the volume of a single grain, D its density, and δ the density of the suspending medium. The resultant downward pull upon a single grain will be $\phi\,(D-\delta)\,g$, where g is the acceleration due to gravity. The volume of liquid between the two levels being $s\,dh$, it follows that the total downward pull upon all the grains included between the two levels must be $ns\,dh\phi\,(D-\delta)\,g$. It is this force which opposes the tendency of the grains to distribute themselves uniformly throughout the entire volume of the suspending medium, or, in other words, it is the force which acts in opposition to the osmotic force $-\frac{2}{3}\,s\,dnE_k$. When equilibrium is established, these two forces must be equal, and we may then write

$$-\tfrac{2}{3}\,s\,dnE_k = ns\,dh\phi\,(D-\delta)\,g. \tag{3}$$

If n_0 and n denote the number of grains per unit of volume at each of two planes h units apart, we obtain, on integrating equation (3),

$$\tfrac{2}{3}\,E_k \log_e n_0/n = \phi\,(D-\delta)\,gh. \tag{4}$$

On substituting in equation (4) the value of E_k in equation (2), and transforming to Briggsian logarithms, we have

$$2.303\,RT/N \log n_0/n = \tfrac{4}{3}\,\pi r^3 g\,(D-\delta)\,h, \tag{5}$$

ϕ being expressed in terms of the mean radius, r, of a single grain. It is evident that if we can measure n, n_0, D, and r in equation (5), the calculation of the Avogadro Constant, N, becomes possible.

The determination of the density of the grains, D, was carried out in two different ways with suspensions of gamboge and mastic which had been rendered uniform by a process of centrifuging. In the first method, the grains were dried to constant weight at 110°, and then by heating to a higher temperature, a viscous liquid was obtained which, on cooling, formed a glassy solid. The density of this solid was determined by suspending it in a solution of potassium bromide of known density.

In the second method for the determination of D, Perrin measured the masses m_1 and m_2 of equal volumes of water and suspension respectively. On evaporating the suspension to dryness, the mass m_3 of suspended solid contained in m_2 grams of suspension was obtained. If the density of water is d, the volume of the suspended grains will be

$$V = \frac{m_1}{d} - \frac{m_2 - m_3}{d},$$

and consequently the density of the grains will be m_3/V. The values of D obtained by these two methods were found to be in excellent agreement.

A microscope furnished with suitable micrometers was employed in the determination of n and n_0. With the high magnification employed, the depth of the field of view was limited: in fact, the measurements were carried out with a microscopic slide similar to those used for counting the corpuscles in the blood. By focussing the microscope at different depths, the average number of grains in the field of view at each level could be counted. Perrin was able to photograph the larger grains at different levels, whereas with the smaller grains it was necessary to reduce the field so that relatively few grains were visible. The average number of grains counted at any two different levels would of course give the desired ratio n_0/n.

The only other quantity in equation (5) to be measured was the average radius of the grains r. To determine this quantity, Perrin made use of a method similar to that used by Thomson for counting the number of electrically charged particles in an ionized gas. Stokes has shown that the force required to impart a uniform velocity v, to a particle of radius r, moving through a liquid medium whose viscosity is η, is given by the formula, $6\,\pi\eta r v$. If the motion be due to gravity, as in the case of suspensions of fine particles, obviously the foregoing expression must be equal to the right-hand side of equation (5), or

$$6\,\pi\eta r v = \tfrac{4}{3}\,\pi r^3\,(D - \delta)\,g.$$

From this equation the value of r can be calculated. The rate at which the grains settled under the influence of gravity was determined by placing a portion of the uniform suspension in a capillary tube and observing the rate at which the suspension cleared, care being taken to keep the temperature constant. This method of determining r was open to the objection that Stokes' law might not apply to particles as small as those of colloidal suspensions.

In order to test the validity of Stokes' law under these conditions, the following modification of the method for the determination of r was introduced. It had been observed that when a suspension is rendered slightly acid, the grains, on coming in contact with the walls of the containing vessel, adhered, while the motion of the grains throughout the bulk of the liquid remained unaltered. In this way it was possible to gradually remove all of the grains from the suspension and count them and, knowing the total volume of suspension taken, the average number of grains per cubic centimeter could be calculated. If the total mass of suspended matter is known, it is an easy matter to calculate the volume of each grain, and from this to compute the radius, r. The value of r determined in this way was found to agree with that calculated by the first method, thus proving the validity of Stokes' law when applied to colloidal suspensions.

Five series of experiments carried out by Perrin with gamboge suspensions in which several thousand individual grains were counted, gave as a mean value of N in equation (5), 69×10^{22}. Similar experiments with mastic suspensions gave $N = 70.0 \times 10^{22}$. These values, it will be seen, are in close agreement with the value of Avogadro's Constant given on page 41.

The Law of Molecular Displacement. The actual movements of the individual grains of a suspension when observed under the microscope are seen to be exceedingly complex and erratic. The horizontal projections of the paths of three different grains in a suspension of mastic are shown in Fig. 72, the dots representing the successive positions occupied by the particles after intervals of 30 seconds. The straight line joining the initial and final positions of a particle is called the *horizontal displacement* Δ, of the particle.

If the time taken by the particle to move from its initial to its final position be t, Einstein * has shown that the mean value of the square of the horizontal displacement of a spherical particle of radius r ought to be

$$\Delta^2 = \frac{RT}{N} \frac{t}{3\,\pi r \eta}, \tag{6}$$

---

* Zeit. Elektrochem., 14, 235 (1908).

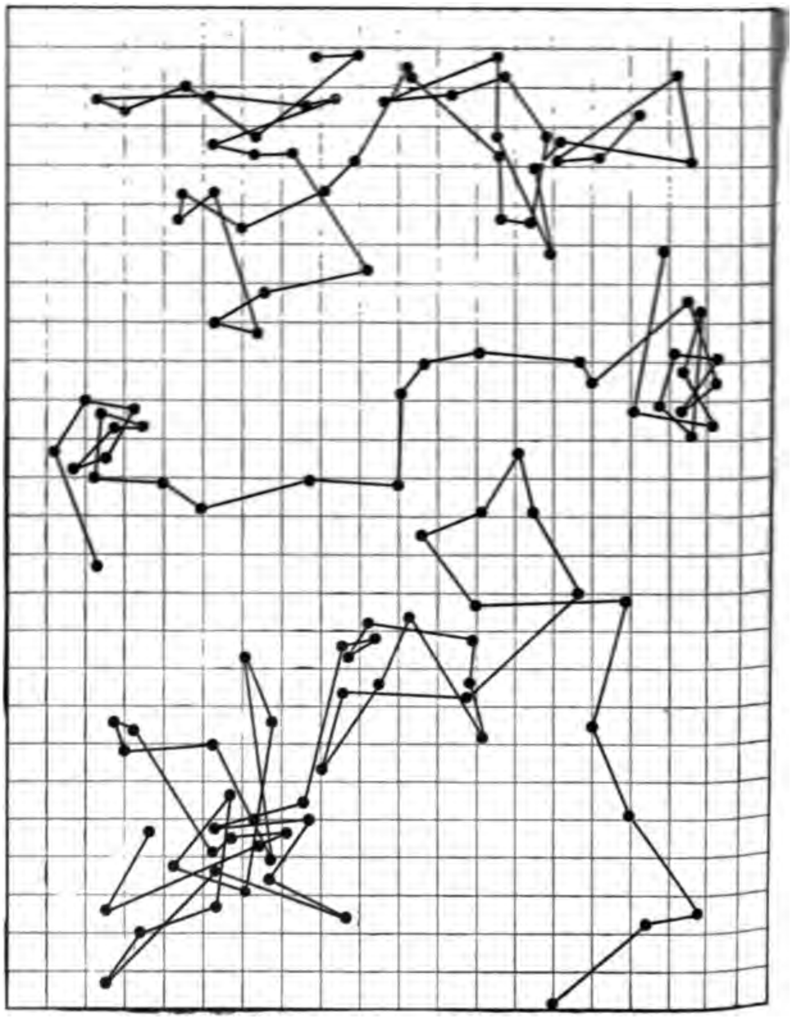


Fig. 72.

where η is the viscosity of the suspending medium and where the other symbols have their usual significance.

This equation was tested by Perrin, using suspensions of gamboge and mastic. Some of the results obtained are given in the following table:

VALUES OF N CALCULATED BY EINSTEIN'S EQUATION.

Suspension.	r in microns.*	$m \times 10^{15}$.	No. of displacements.	$N \times 10^{-22}$.
Gamboge in water..............	0.367	246	1500	69
Gamboge in 10% solution of glycerine	0.385	290	100	64
Mastic in water.................	0.52	650	1000	73
Mastic in 27% solution of urea ..	5.50	750,000	100	78

* The micron is one-millionth of a meter or one ten-thousandth of a centimeter.

It will be seen that notwithstanding the large variations in the granular masses of the different suspensions recorded in the table, the values of N, calculated by means of Einstein's equation, are quite concordant. Perrin gives as the mean value of all of his experiments, $N = 68.5 \times 10^{22}$.

Recent Investigations of the Brownian Movement. Nordlund * has recently repeated Perrin's experiments, employing a colloidal solution of mercury and an arrangement of apparatus whereby the movements of the particles could be recorded photographically. The mean value of N derived from twelve carefully executed experiments was 59×10^{22}, the average deviation of the results of the individual experiments from the mean being approximately 10 per cent.

The Brownian Movement in gases has been studied by Millikan † and by Fletcher ‡ employing a minute drop of oil as the suspended particle. In the gaseous state, where the intermolecular distances are greater than in the liquid state, not only are the collisions less frequent but the mean free paths are appreciably longer. These conditions are favorable to the study of the Brownian Movement and offer an opportunity for the determination of the Avogadro Constant with a high degree of accuracy. As the mean of nearly ix thousand measurements, Fletcher gives $N = 60.3 \times 10^{22}$, this value being accurate to within 1.2 per cent.

---

* Zeit. phys. Chem., **87**, 60 (1914). † Phys. Rev., **1**, 220 (1913).
‡ *Ibid.*, **4**, 453 (1914).

CHAPTER XIV.

THERMOCHEMISTRY.

General Introduction. A chemical reaction is almost invariably accompanied by a thermal change. In the majority of cases heat is evolved; a violent reaction developing a large amount of heat, while a feeble reaction develops a comparatively small amount. Such reactions are said to be *exothermic.* A relatively small number of chemical reactions are known which take place with an absorption of heat. These are termed *endothermic* reactions. Instances of chemical reactions unaccompanied by any thermal change are very rare and are almost wholly confined to the reciprocal transformations of optical isomers. These facts, which were first observed by Boyle and Lavoisier, led to the view that the amount of heat evolved in a chemical reaction might be taken as a measure of the chemical affinity of the reacting substances. However, with the advance of our theoretical knowledge, it is now known that this is not true, although a parallelism between heat evolution and chemical affinity frequently exists.

Thermochemistry is concerned with the thermal changes which accompany chemical reactions.

Thermal Units. Heat is a form of energy, and like other forms of energy it may be resolved into two factors; an intensity factor, the temperature, and a capacity factor, which may be measured in any one of several units. Among these units those defined below are the most frequently employed.

The *small calorie* (cal.) is the quantity of heat required to raise the temperature of 1 gram of water from 15° C. to 16° C. The temperature interval is specified because the specific heat of water varies with the temperature. The *large or kilogram calorie* (Cal.) is the quantity of heat required to raise the temperature of 1000 grams of water from 15° C. to 16° C. The *Ostwald or average* *calorie* (K), is the quantity of heat required to raise the temperature of 1 gram of water from the melting point of ice to the boiling point of water under a pressure of 760 mm. of mercury. It is approximately equal to 100 cal. or to 0.1 Cal. The *joule* (j), a unit based on the C.G.S. system, is equal to 10^7 ergs. This being inconveniently small is generally multipled by 1000, giving the *kilojoule* (J), which is therefore equal to 10^{10} ergs. The last two units are open to the objection that their values are dependent upon the mechanical equivalent of heat, any change in the accepted value of which would involve a correction of the unit of heat. The different capacity factors of heat energy are related as follows: —

$$1 \text{ cal.} = 0.001 \text{ Cal.} = 0.01 \text{ K (approx.)} = 4.183 \text{ j} = 0.004183 \text{ J}.$$

Thermochemical Equations. In order to represent the changes in energy which accompany chemical reactions, an additional meaning has been assigned to the chemical symbols. As ordinarily used, these symbols represent only the molecular or formula weights of the reacting substances. In a thermochemical or energy equation the symbols represent not only the weight in grams expressed by the formula weights of the substances, but also the amount of heat energy contained in the formula weight in one state as compared with the energy contained in a standard state. For example, the energy equation,

$$C + 2\,O = CO_2 + 94{,}300 \text{ cal.},$$

indicates that the energy contained in 12 grams of carbon and 32 grams of oxygen exceeds the energy contained in 44 grams of carbon dioxide, at the same temperature, by 94,300 calories. In writing energy equations it is very essential that we have some means of distinguishing between the different states of aggregation of the reacting substances, since the energy content of a substance is not the same in the gaseous, liquid, and solid states. In the system proposed by Ostwald, ordinary type is used for liquids, heavy type for solids, and italics for gases. Another and more convenient system has been proposed, in which solids are designated by enclosing the symbol or formula within square brackets; liquids by the simple, unbracketed symbol or formula;

and gases by enclosing the symbol or formula within parentheses. The above equation should, therefore, be written in the following manner: —

$$[C] + (2\ O) = (CO_2) + 94{,}300 \text{ cal.}$$

Thermochemical Measurements. In order to measure the number of calories evolved or absorbed when substances react, it is necessary that the reaction should proceed rapidly to completion. This condition is fulfilled by two classes of processes. In the first class we may mention the processes of solution, hydration, and neutralization; and in the second class, the process of combustion.

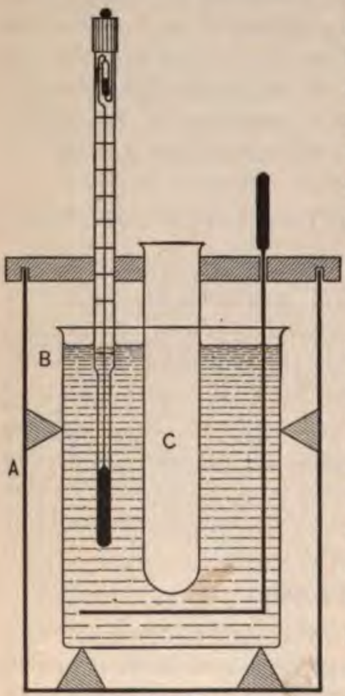


Fig. 73.

The apparatus used for measuring the capacity factor of heat energy is a *calorimeter*. This instrument may be given a variety of forms, depending upon the particular use to which it is to be put. A simple form of calorimeter is shown in Fig. 73. It consists of two concentric metal cylinders, *A* and *B*, insulated from each other by an air jacket, the inner vessel being supported on vulcanite points. Through a vulcanite cover passes a thin walled test tube, in which the reaction is allowed to take place. An accurate thermometer and a ring-stirrer also pass through the cover of the calorimeter. In order to determine the thermal capacity of the calorimeter, *B* is nearly filled with water, and a known mass of water, m, at a temperature t_1 is introduced into C. Let the initial temperature of the water in B be t_2. The water in B is stirred until the contents of both B and C have acquired the same temperature, t_3. When thermal equilibrium has been established, it is evident that $m\,(t_1 - t_3)$ calories are required to raise the temperature of the apparatus and the water in B, $(t_2 - t_3)$ degrees. From this data it is an easy matter to calculate the number of calories required to raise the temperature of the apparatus and water in B 1 degree, this being the thermal capacity of the apparatus. The calorimeter may now be used to determine the heat evolved or absorbed in a reaction. Suppose, for example, that it is desired to measure the heat of neutralization of an acid by a base. Equivalent quantities of both acid and base are dissolved in equal volumes of water, care being taken to make the solutions dilute. A definite volume of one solution is introduced into C and an equal volume of the other solution is placed in a vessel from which it can be quickly and completely transferred to C. When both solutions have acquired the same temperature, the thermometer in B is read and then the two solutions are mixed. When the reaction is complete, the temperature of the water in B is again noted. If the thermal capacity of the calorimeter is Q, and the rise in temperature produced by the reaction is θ, then $Q\theta$ is the amount of heat evolved by the reaction. To this quantity of heat must be added the number of calories required to raise the temperature of the products of the reaction θ degrees. The solutions of the products being dilute, their specific heats may be assumed to be equal to unity. From the total quantity of heat so obtained, the number of calories evolved when molecular quantities react can be readily calculated. The chief source of error in calorimetric measurements is loss by radiation. This may be reduced to a minimum (1) by making the thermal capacity of the calorimeter large, and (2) by so arranging matters that the initial temperature of the water in the calorimeter is as much below the temperature of the room as the final temperature is above it.

The Combustion Calorimeter. The combustion of many substances, such as organic compounds, proceeds very slowly in air under ordinary pressures. Such reactions can be accelerated, if they are caused to take place in an atmosphere of compressed oxygen. For this purpose the combustion calorimeter was devised by Berthelot.* In this apparatus the essential feature is

* Ann. Chim. Phys., (5), **23**, 160 (1881); (6), **10**, 433 (1887).

the so-called *combustion bomb*, shown in Fig. 74. This consists of a strong steel cylinder lined with platinum or gold, and furnished with a heavy threaded cover. The substance to be burned is placed in a platinum capsule fastened to the support *R*, and a short piece of fine iron wire of known mass is connected with the electric terminals *Z*, *Z*, the middle portion of the wire dipping into the substance. The cover is then screwed down tight, and the bomb is filled with oxygen under a pressure of from 20 to 25 atmospheres. The bomb is then submerged in the calorimeter, as shown in Fig. 75. The mass of water in the calorimeter being known and its temperature having been read, an electric current is passed through the iron wire in the bomb causing it to burn and thus ignite the substance. The rise in temperature due to the combustion is observed, and the quantity of heat evolved is calculated. Corrections must be applied for loss by radiation, for the heat evolved from the combustion of the iron, and for the heat evolved from the oxidation of the nitrogen of the residual air in the bomb.

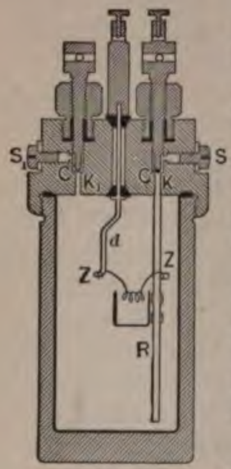


Fig. 74.

For the details of the method of determining heats of combustion the student must consult a laboratory manual.

Law of Lavoisier and Laplace. In 1780, Lavoisier and Laplace,[*] as a result of their thermochemical investigations, enunciated the following law: — *The quantity of heat which is required to decompose a chemical compound is precisely equal to that which was evolved in the formation of the compound from its elements.* This first law of thermochemistry will be seen to be a direct corollary of the law of the conservation of energy which was first clearly stated by Mayer in 1842.

Law of Constant Heat Summation. A generalization of fundamental importance to the science of thermochemistry was discovered in 1840 by Hess.[†] He pointed out that *the heat evolved in a*

---

[*] Oeuvres de Lavoisier, Vol. II, p. 283.

[†] Pogg. Ann., 50, 385 (1840).

chemical process is the same whether it takes place in one or in several steps. This is known as *the law of constant heat summation.* The truth of the law may be illustrated by the equality of the heat of formation of ammonium chloride in aqueous solution, when prepared in two different ways.

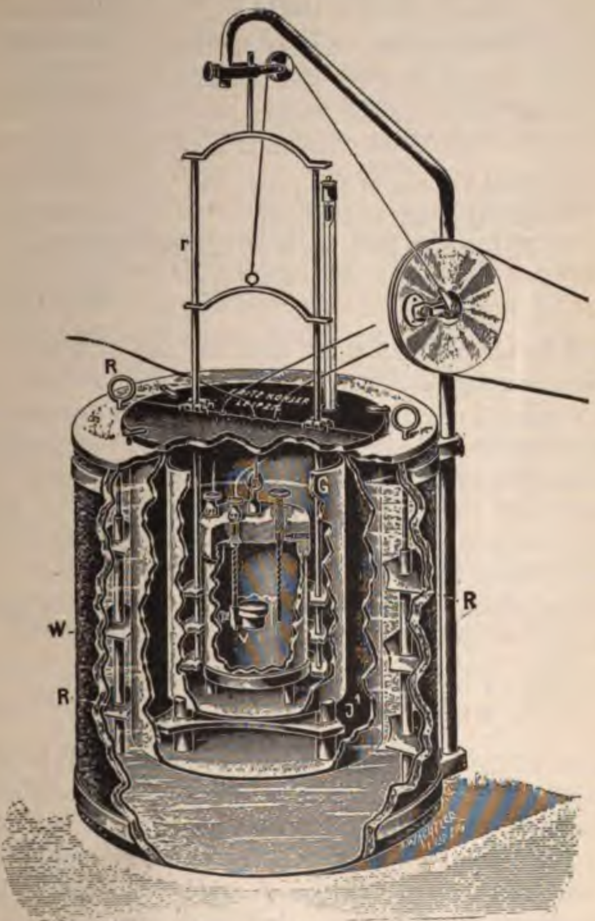


Fig. 75.

Thus,

(A)

$$\begin{array}{ll} (NH_3) + (HCl) = {[NH_4Cl]} & +42{,}100 \text{ cal.} \\ {[NH_4Cl]} + \text{aq.} = NH_4Cl, \text{ aq.} & -\ 3{,}900 \text{ cal.} \\ \cline{2-2} & 38{,}200 \text{ cal.} \end{array}$$

(B)

$$\begin{array}{ll} (NH_3) + \text{aq.} = NH_3, \text{ aq.} & +\ 8{,}400 \text{ cal.} \\ (HCl) + \text{aq.} = HCl, \text{ aq.} & +17{,}300 \text{ cal.} \\ NH_3, \text{ aq.} + HCl, \text{ aq.} = NH_4Cl, \text{aq.} & +12{,}300 \text{ cal.} \\ \cline{2-2} & 38{,}000 \text{ cal.} \end{array}$$

It will be observed that the total amount of heat evolved in the formation and solution of ammonium chloride is the same within the limits of experimental error, whether gaseous ammonia and hydrochloric acid are allowed to react and the resulting product is dissolved in water, or whether the gases are each dissolved separately and then allowed to react. It should be noted that when a substance is dissolved in so much water that the addition of more water or the removal of a small portion of water produces no thermal effect, it is customary to denote it by the symbol aq. (Latin *aqua* = water). Thus,

$$NH_4Cl, \text{ aq.} + nH_2O = NH_4Cl, \text{ aq.},$$
$$NH_4Cl, \text{ aq.} - nH_2O = NH_4Cl, \text{ aq.}$$

By means of the law of constant heat summation it is possible to find indirectly the amount of heat developed or absorbed by any reaction, even though it is impossible to carry it out experimentally. For example, it is impossible to measure the heat evolved when carbon burns to carbon monoxide. But the heat evolved when carbon monoxide burns to carbon dioxide, and also the heat evolved when carbon burns to carbon dioxide, can be accurately determined. The energy equations are as follows: —

$$[C] + 2(O) = (CO_2) + 94{,}300 \text{ cal.} \qquad (1)$$
$$(CO) + (O) = (CO_2) + 67{,}700 \text{ cal.} \qquad (2)$$

Treating these equations algebraically, and subtracting equation (2) from equation (1), we have

$$[\mathrm{C}] + (\mathrm{O}) = (\mathrm{CO}) + 26{,}600 \text{ cal.},$$

or, the heat of combustion of carbon to carbon monoxide is 26,600 calories. Again, as a further illustration of the applicability of the law of Hess, we may take the calculation of the heat of formation of hydriodic acid from its elements, making use of the following energy equations: —

$$2\,\mathrm{KI, aq.} + 2\,(\mathrm{Cl}) = 2\,\mathrm{KCl, aq.} + 2\,[\mathrm{I}] + 524\ \mathrm{K} \qquad (1)$$

$$2\,\mathrm{HI, aq.} + 2\,\mathrm{KOH, aq.} = 2\,\mathrm{KI, aq.} + 2\,\mathrm{H_2O} + 274\ \mathrm{K} \qquad (2)$$

$$2\,\mathrm{HCl, aq.} + 2\,\mathrm{KOH, aq.} = 2\,\mathrm{KCl, aq.} + 2\,\mathrm{H_2O} + 274\ \mathrm{K} \qquad (3)$$

$$2\,(\mathrm{HI}) + \mathrm{aq.} = 2\,\mathrm{HI, aq.} + 384\ \mathrm{K}, \qquad (4)$$

$$2\,(\mathrm{HCl}) + \mathrm{aq.} = 2\,\mathrm{HCl, aq.} + 346\ \mathrm{K}, \qquad (5)$$

$$2\,(\mathrm{H}) + 2\,(\mathrm{Cl}) = 2\,(\mathrm{HCl}) + 440\ \mathrm{K}, \qquad (6)$$

adding equations (1) and (2),

$$2\,(\mathrm{Cl}) + 2\,\mathrm{HI, aq.} + 2\,\mathrm{KOH, aq.} = 2\,\mathrm{KCl, aq.} + 2\,[\mathrm{I}] + 2\,\mathrm{H_2O} + 798\ \mathrm{K}. \qquad (7)$$

Subtracting equation (3) from equation (7),

$$2\,(\mathrm{Cl}) + 2\,\mathrm{HI, aq.} - 2\,\mathrm{HCl, aq.} = 2\,[\mathrm{I}] + 524\ \mathrm{K},$$

or

$$2\,(\mathrm{Cl}) + 2\,\mathrm{HI, aq.} = 2\,[\mathrm{I}] + 2\,\mathrm{HCl, aq.} + 524\ \mathrm{K}, \qquad (8)$$

adding equations (4) and (8),

$$2\,(\mathrm{HI}) + \mathrm{aq.} + 2\,(\mathrm{Cl}) = 2\,[\mathrm{I}] + 2\,\mathrm{HCl, aq.} + 908\ \mathrm{K}, \qquad (9)$$

subtracting equation (5) from equation (9),

$$2\,(\mathrm{HI}) + 2\,(\mathrm{Cl}) - 2\,(\mathrm{HCl}) = 2\,[\mathrm{I}] + 562\ \mathrm{K},$$

or

$$2\,(\mathrm{HI}) + 2\,(\mathrm{Cl}) = 2\,[\mathrm{I}] + 2\,(\mathrm{HCl}) + 562\ \mathrm{K}, \qquad (10)$$

subtracting equation (6) from equation (10),

$$2\,(\mathrm{HI}) - 2\,(\mathrm{H}) = 2\,[\mathrm{I}] + 122\ \mathrm{K}, \quad ✓$$

or

$$2\,(\mathrm{H}) + 2\,(\mathrm{I}) = 2\,(\mathrm{HI}) - 122\ \mathrm{K}.$$

In a similar manner, practically any heat of formation may be calculated, provided the proper energy equations are combined.

Heat of Formation. The intrinsic energy of the substances entering into chemical reaction is unknown, the amount of heat evolved or absorbed in the process being simply a measure of the difference between the energy of the reacting substances and the energy of the products of the reaction. Thus, in the equation

$$[C] + 2\,(O) = (CO_2) + 94{,}300 \text{ cal.},$$

the difference between the energy of a mixture of 12 grams of carbon and 32 grams of oxygen, and the energy of 44 grams of carbon dioxide is seen to be 94,300 calories. The equation is clearly incomplete since we have no means of determining the intrinsic energies of free carbon and oxygen. Furthermore, since the elements are not mutually convertible, we have no means of determining the difference in energy between them. It is customary, therefore, in view of this lack of knowledge, to put the intrinsic energies of the elements equal to zero.

If the heats of formation of the substances present in a reaction are known, it is much simpler to substitute these in the energy equation and solve for the unknown term. This method avoids the laborious process of elimination from a large number of energy equations, as in the preceding pages. If all of the substances involved in a reaction are considered as decomposed into their elements, it is evident that the final result of the reaction will be the difference in the sums of the heats of formation on the two sides of the equation. This leads to the following rule: — *To find the quantity of heat evolved or absorbed in a chemical reaction, subtract the sum of the heats of formation of the substances initially present from the sum of the heats of formation of the products of the reaction, placing the heat of formation of all elements equal to zero.*

The energy equation for the formation of carbon dioxide from its elements may then be written as follows: —

$$0 + 0 = (CO_2) + 94{,}300 \text{ cal.},$$

or

$$(CO_2) = -\ 94{,}300 \text{ cal.}$$

That is, the energy of 1 mol of carbon dioxide is −94,300 calories. Therefore in writing an energy equation we make use of the following rule: — *Replace the formulas of each compound in the equation representing the reaction by the negative values of their respective heats of formation and solve for the unknown term.* This unknown term may be either the heat of a reaction or the heat of formation of one of the reacting substances. The following examples will serve to illustrate the application of the above rules: —

(1) Let it be required to find the heat of the following reaction

$$[MgCl_2] + 2\,[Na] = 2\,[NaCl] + [Mg] + x,$$

where x is the heat of the reaction. The heat of formation of $MgCl_2$ is 151 Cal., and that of NaCl is 97.9 Cal., therefore,

$$-\,151 + 0 = -\,(2 \times 97.9) + 0 + x,$$

or

$$x = 44.8 \text{ Cal.}$$

(2) The heat of combustion of 1 mol of methane is 213.8 Cal., and the heats of formation of the products, carbon dioxide and water, are 94.3 Cal. and 68.3 Cal., respectively. Let it be required to find the heat of formation of methane. Representing the heat of formation of methane by x, we have

$$(CH_4) + 2\,(O_2) = (CO_2) + 2\,(H_2O) + 213.8 \text{ Cal.},$$

$$-\,x + 0 = -\,94.3 - 2 \times 69.3 + 213.8,$$

or

$$x = 17.1 \text{ Cal.}$$

(3) The heat of combustion of 1 mol of carbon disulphide is 265.1 Cal., the thermochemical equation being

$$CS_2 + 3\,(O_2) = (CO_2) + 2\,(SO_2) + 265.1 \text{ Cal.}$$

The heats of formation of carbon dioxide and sulphur dioxide are 94.3 Cal. and 71 Cal. respectively. The heat of formation of carbon disulphide x, may then be calculated as follows: —

$$-\,x + 0 = -\,94.3 - 2 \times 71 + 265.1,$$

or

$$x = -28.8 \text{ Cal.}$$

Carbon disulphide is thus seen to be an endothermic compound.

Heat of Solution. The thermal change accompanying the solution of 1 mol of a substance in so large a volume of solvent that subsequent dilution of the solution causes no further thermal change is termed the *heat of solution*. The solution of neutral salts is generally an endothermic process. This fact may be readily accounted for on the hypothesis that considerable heat

HEATS OF FORMATION AND SOLUTION.

Substance.	Heat of Formation.	Heat of Solution.
Water, vapor	58.7	....
Water, liquid	68.4	....
Hydrochloric acid	22.0	20.3
Sulphuric acid	193.1	17.8
Ammonia	12.0	8.4
Nitric acid	41.9	7.2
Phosphoric acid	302.9	2.7
Potassium hydroxide	103.2	13.3
Potassium chloride	104.3	−3.1
Potassium bromide	95.1	−5.1
Potassium iodide	80.1	−5.1
Potassium nitrate	119.5	−8.5
Sodium hydroxide	101.9	10.9
Sodium chloride	97.6	1.2
Sodium bromide	85.6	−0.2
Sodium sulphate	328.8	0.2
Sodium nitrate	111.3	−5.0
Sodium carbonate	272.6	5.6
Ammonium chloride	75.8	−4.0
Ammonium nitrate	88.0	−6.2
Calcium hydroxide	215.0	3.0
Calcium chloride	170.0	17.4
Magnesium sulphate	502.0	20.3
Ferrous chloride	82.0	17.9
Ferric chloride	96.1	63.3
Zinc chloride	97.0	15.6
Zinc sulphate	30.0	18.5
Cadmium chloride	293.2	3.0
Cupric chloride	51.6	11.1
Cupric sulphate	182.6	15.8
Mercuric chloride	53.2	−3.3
Silver nitrate	28.7	−5.4
Stannous chloride	80.8	0.3
Stannic chloride	127.3	29.9
Lead chloride	82.8	−6.8
Lead nitrate	105.5	−7.6

must be absorbed as heat of fusion and heat of vaporization before the solid salt can assume a condition in solution which closely resembles that of a gas. The heat of solution of hydrated salts is less than the heat of solution of the corresponding anhydrous salts. For example, the heat of solution of 1 mol of anhydrous calcium nitrate is 4000 calories, while the heat of solution of 1 mol of the tetrahydrate is −7600 calories. The difference between the heats of solution of the anhydrous and hydrated salts is termed the *heat of hydration*. The heats of formation and heats of solution in water of some of the more common compounds are given in the preceding table, the values being expressed in large calories.

Heat of Dilution. The *heat of dilution* of a solution is the quantity of heat per mol of solute which is evolved or absorbed when the solution is greatly diluted. Beyond a certain dilution, further addition of solvent produces no thermal change. While there is a definite heat of solution for a particular solute in a particular solvent, the heat of dilution remains indefinite, since the latter is dependent upon the degree of dilution. Those gases which obey Henry's law are practically the only substances which have no appreciable heats of solution or dilution.

The following tables give the heats of dilution of hydrochloric and nitric acids.

HEAT OF DILUTION OF SOLUTIONS OF HYDROCHLORIC ACID.

Heat of solution = 20.3 cal.

$HCl+H_2O$	5.37
$HCl+2\ H_2O$	11.36
$HCl+10\ H_2O$	16.16
$HCl+50\ H_2O$	17.1
$HCl+300\ H_2O$	17.3

HEAT OF DILUTION OF SOLUTIONS OF NITRIC ACID.

Heat of solution = 7.15 cal.

HNO_3+H_2O	3.84
$HNO_3+2\ H_2O$	2.32
$HNO_3+4\ H_2O$	1.42
$HNO_3+6\ H_2O$	0.2
$HNO_3+8\ H_2O$	−0.04
$HNO_3+100\ H_2O$	−0.03

Reactions at Constant Volume. When a chemical reaction takes place without any change in volume, or when the external work resulting from a change in volume is not included in the heat of the reaction, the process is said to take place at constant volume. That is to say, the condition of constant volume is a condition which involves no external work, either positive or negative. Under these conditions the total energy of the reacting substances is equal to the total energy of the products of the reaction, plus the quantity of heat developed by the reaction.

Reactions at Constant Pressure. When a chemical reaction is accompanied by a change in volume, the system suffers a loss of heat equivalent to the work done against the atmosphere, if the volume increases; or the system gains an amount of heat equivalent to the work done on the system by the atmosphere, if the volume decreases. Under these conditions the reaction is said to take place at constant pressure. The difference between constant volume and constant pressure conditions, then, is that under the former, the heat equivalent of the work corresponding to any change in volume which may occur is not considered as having any effect upon the energy of the system; whereas under the latter, due account is taken of the change in energy resulting from change in volume. Suppose that in a reaction, 1 mol of gas is formed. Under standard conditions of temperature and pressure the volume of the system will be increased by 22.4 liters. The formation of gas involves the performance of work against the atmosphere, this work being done at the expense of the heat energy of the system. To calculate the heat equivalent of the work done, let us imagine the gas enclosed in a cylinder fitted with a piston whose area is 1 square centimeter. The normal pressure of the atmosphere on the piston is 76 cm. of mercury or 1033.3 grams per square centimeter. If the increase in the volume of the gas is 22.4 liters, the piston will be raised through 22,400 cm. and the work done will be $1033.3 \times 22{,}400$ gram-centimeters. The heat equivalent of this change in volume will be $(1033.3 \times 22{,}400) \div 42{,}600 = 542.3$ calories or 0.5423 large calories. This amount of heat must be added to the heat of the reaction. It should be observed that this correction is independent of the actual value of the pressure upon the system. Thus, if the pressure is increased n times, the volume of the gas will be reduced to $1/n$ of its former value, and the work done will involve moving the piston through $1/n$ of the distance against an n-fold pressure, which is plainly equivalent to the former amount of work. While the correction is independent of the pressure it is not independent of the temperature. The familiar equation, $pv = RT$, shows us that the work done by a gas is directly proportional to its absolute temperature. Thus, if a gas is evolved at 273° absolute, it will occupy double the volume it would occupy at 0°, and the work done at 273° will involve moving the piston through twice the distance that it would have to be moved at 0°. Theoretically, a gas evolved at the absolute zero would occupy no volume and hence no work would be done. Introducing the correction for temperature, we see that

$$\frac{542.3}{273} \times T = 1.986\,T \text{ cal.},$$

must be added to the heat of the reaction, where T is the absolute temperature at which the change in volume occurs. For all ordinary purposes it is sufficiently accurate to take $2\,T$ calories as the correction. Thus, suppose n mols of gas to be formed in a reaction at 17° C., the amount of heat absorbed will be

$$n \times 2\,(273 + 17) = 580\,n \text{ cal.}$$

Under constant pressure conditions, the symbols, in addition to their usual significance, represent the energy plus or minus the term, $2\,T$ per mol, the positive or negative sign being used according as the gas is absorbed or formed. Since the constant volume condition is a condition in which no account is taken of the external work, even if a change in volume does occur during the reaction, and the constant pressure condition is one in which the external work is taken into consideration, it is apparent that the relation of the heat energy of a reaction at constant volume, Q_v, to the heat energy at constant pressure Q_p, can be represented by the equation

$$Q_p = Q_v - 2\,nT \text{ cal.},$$

where n denotes the number of mols of gas formed in excess of those initially present. This equation is of great importance in connection with the determination of heats of combustion in the bomb-calorimeter in which the reactions necessarily take place under constant volume conditions. Since it is customary to state heats of reaction under constant pressure conditions, the foregoing equation makes it possible to convert heats of combustion determined under constant volume conditions into heats of combustion under constant pressure conditions. For example, the combustion of naphthalene takes place in accordance with the equation

$$C_{10}H_8 + 12\,(O_2) = 10\,(CO_2) + 4\,(H_2O) + 1242.95 \text{ Cal.}$$

It is apparent that the combustion is accompanied by the formation of 2 mols of gas, and at 15° C. the correction will be

$$Q_p = 1242.95 - 2 \times 0.002\,(273 + 15),$$

or

$$Q_p = 1241.8 \text{ Cal.}$$

The volume occupied by solids or liquids is so small as to be negligible and does not enter into these calculations.

Variation of Heat of Reaction with Temperature. If a chemical reaction be allowed to take place first at the temperature t_1, and then at the temperature t_2, the amounts of heat developed in the two cases will be found to be quite different. Let Q_1 and Q_2 represent the quantities of heat evolved at the temperatures t_1 and t_2, respectively. Let us imagine that the reaction takes place at the temperature t_1, Q_1 units of heat being evolved; and then let the products of the reaction be heated to the temperature t_2. If c' represents the total thermal capacity of the products of the reaction, then the quantity of heat necessary to produce this rise in temperature will be $c'\,(t_2 - t_1)$. Now let us imagine the reacting substances, at the temperature t_1, to be heated to the temperature t_2, and then allowed to react with the evolution of Q_2 units of heat. The heat necessary to produce this rise in temperature in the reacting substances is $c\,(t_2 - t_1)$, where c is the total thermal capacity of the original substances. Having started with the same substances at the same initial temperature, and having obtained the same products at the same final temperature, we have, according to the law of the conservation of energy,

$$Q_1 - c'(t_2 - t_1) = Q_2 - c(t_2 - t_1),$$

or

$$\frac{Q_2 - Q_1}{t_2 - t_1} = c - c',$$

or, where the change in temperature is very small,

$$\frac{dQ}{dt} = c - c'.$$

If c' is greater than c then the sign of dQ/dt will be negative, or, in other words, an increase in temperature will cause a decrease in the heat of reaction. On the other hand, if c is greater than c', dQ/dt will be positive and the heat of reaction will increase with the temperature.

Example. The reaction between hydrogen and oxygen at 18° C. is represented by the following equation: —

$$2\,(H_2) + (O_2) = 2\,(H_2O) + 1367.1\text{ K}.$$

Suppose it is required to find how much heat will be evolved when equal masses of the two gases react at 110° C., the product of the reaction being maintained at this temperature, and the pressure remaining constant. The specific heats per gram of the different substances involved are as follows: —

Hydrogen = 3.409; Oxygen = 0.2175; Water (between 18° and 100°) = 1; Water (between 100° and 110°) = 0.5.

The heat of vaporization of water is 537 calories per gram.

For liquid water per degree we have,

$$dQ/dt = (4 \times 3.409 + 32 \times 0.2175) - (36 \times 1) = -\,15.404\text{ cal.}$$

and for (100° − 18°) = 82°, we have, $82 \times (-15.404) = -1263$ cal. The heat of formation of liquid water at 100° is, therefore,

$$1367.1 - 12.63 = 1354.47\text{ K}.$$

When the liquid water is vaporized at 100°, (36 × 537) calories of this heat is absorbed, or the formation of steam at 100° from hydrogen and oxygen, evolves

$$1354.47 - 193.32 = 1161.15\text{ K}.$$

For steam per degree, we have,

$$dQ/dt = (4 \times 3.409 + 32 \times 0.2175) - (36 \times 0.5) = 2.596 \text{ cal.},$$

and for the interval $(110° - 100°) = 10°$,

$$10 \times 2.596 = 25.96 \text{ cal.}$$

Or for the total heat evolved, we have

$$1161.15 + 0.2596 = 1161.41 \text{ K.}$$

Heat of Combustion. The heat evolved during the complete oxidation of unit mass of a substance is termed its *heat of combustion.* The unit of mass commonly chosen in all physico-chemical calculations is the mol. An enormous amount of experimental work has been done by Thomsen,* Berthelot,† and Langbein ‡ on the determination of the heats of combustion of a large number of organic compounds. A few of their results are given in the accompanying tables.

SATURATED HYDROCARBONS.

Hydrocarbon.	Heat of Combustion.	Difference.
	Cal.	Cal.
Methane, CH_4	211.9	
Ethane, C_2H_6	370.4	158.5
Propane, C_3H_8	529.2	158.8
Butane, C_4H_{10}	687.2	158.0
Pentane, C_5H_{12}	847.1	159.9

UNSATURATED HYDROCARBONS.

Hydrocarbon.	Heat of Combustion.	Difference.
	Cal.	Cal.
Ethylene, C_2H_4	333.4	
Propylene, C_3H_6	492.7	159.3
Isobutylene, C_4H_8	650.6	157.9
Amylene, C_5H_{10}	807.6	157.0
Acetylene, C_2H_2	310.1	
Allylene, C_3H_4	467.6	157.5

---

* Thermochemische Untersuchungen, 4 Vols.

† Essai de Mecanique Chimique, Thermochimie, Donées et Lois Numeriques.

‡ Jour. prakt. Chem., 1885 to 1895.

ALCOHOLS.

Alcohol.	Heat of Combustion.	Difference.
	Cal.	Cal.
Methyl alcohol, CH_4O	182.2	
Ethyl alcohol, C_2H_6O	340.5	158.3
Propyl alcohol, C_3H_8O	498.6	158.1
Isobutyl alcohol, $C_4H_{10}O$	658.5	159.9

It will be observed that a very nearly constant difference in the heat of combustion corresponds to a constant difference of a CH_2 group in composition. A number of interesting relations between heats of combustion of compounds and their differences in composition have been discovered, but these cannot be taken up at this time. It has also been pointed out that the heat of combustion of organic compounds is conditioned not only by their composition, but also by their molecular constitution.

Some exceedingly interesting and important results have been obtained with the different allotropic forms of the elements. For example, when equal masses of the three common allotropic forms of carbon are burned in oxygen, the amounts of heat evolved are found to be quite different, as is shown by the following energy equations: —

$$[C]\text{ diamond} + 2\,(O) = (CO_2) + 94.3\text{ Cal.}$$
$$[C]\text{ graphite} + 2\,(O) = (CO_2) + 94.8\text{ Cal.}$$
$$[C]\text{ amorphous} + 2\,(O) = (CO_2) + 97.65\text{ Cal.}$$

It is apparent that amorphous carbon contains the greatest amount of energy of any one of the three allotropic modifications, and, therefore, when amorphous carbon is changed into diamond, the reaction must be accompanied by the evolution of $(97.65 - 94.3) = 3.35$ Cal. In like manner, the allotropic forms of sulphur and phosphorus have different heats of combustion. The following equations show the heat equivalents of the differences in intrinsic energy between the allotropic forms: —

$$S\text{ (monoclinic)} = S\text{ (rhombic)} + 2.3\text{ Cal.}$$
$$P\text{ (white)} = P\text{ (red)} + 3.71\text{ Cal.}$$

When the same substance is burned in oxygen and then in ozone, it is found that more heat is evolved in ozone than in oxygen. The energy equation expressing the change of ozone into oxygen may be written thus,

$$(O_3) = 1\tfrac{1}{2}\,(O_2) + 36.2 \text{ Cal.}$$

All of the above facts illustrate the general principle that the larger amounts of intrinsic energy are associated with the more unstable forms.

Thermoneutrality of Salt Solutions. In addition to the law of constant heat summation, Hess discovered two other important laws of thermochemistry, *viz.*, the law of thermoneutrality of salt solutions, and the law governing the neutralization of acids by bases.* When two dilute salt solutions are mixed there is neither evolution nor absorption of heat. Thus when dilute solutions of sodium nitrate and potassium chloride are mixed, there is no thermal effect. The energy equation may be written as follows:—

$$NaNO_3, \text{aq.} + KCl, \text{aq.} = NaCl, \text{aq.} + KNO_3, \text{aq.} + 0 \text{ Cal.}$$

According to this equation a double decomposition has taken place and we should naturally expect an evolution or an absorption of heat. While Hess could not account for the absence of any thermal effect, he recognized the fact as quite general and formulated the law of the thermoneutrality of salt solutions as follows:—*The metathesis of neutral salts in dilute solutions takes place with neither evolution nor absorption of heat.*

The explanation of the phenomenon of thermoneutrality was furnished by the theory of electrolytic dissociation. When the above equation is written in the ionic form, it becomes

$$Na^{\cdot} + NO_3{}' + K^{\cdot} + Cl' = Na^{\cdot} + Cl' + K^{\cdot} + NO_3{}'.$$

From this it is apparent that the same ions exist on both sides of the equation, and in reality no reaction takes place.

There are numerous exceptions to the law of thermoneutrality. These can be satisfactorily accounted for by the theory of electrolytic dissociation. All of those salts, the behavior of which in dilute solution is contrary to the law, are found to be only partially ionized, and, therefore, when their solutions are mixed, a chemical reaction actually occurs. The exceptions must be considered as furnishing additional evidence in favor of the theory of electrolytic dissociation.

---

* Pogg. Ann., 50, 385 (1840).

Heat of Neutralization. Hess also discovered * that when dilute solutions of equivalent quantities of strong acids and strong bases are mixed, practically the same amount of heat is evolved. The following energy equations may be considered as typical examples of such neutralizations: —

$$\text{HCl, aq.} + \text{NaOH, aq.} = \text{NaCl, aq.} + H_2O + 13.75 \text{ Cal.,}$$
$$HNO_3\text{, aq.} + \text{NaOH, aq.} = NaNO_3 \text{ aq.} + H_2O + 13.68 \text{ Cal.,}$$
$$\text{HCl, aq.} + \text{KOH, aq.} = \text{KCl, aq.} + H_2O + 13.70 \text{ Cal.,}$$
$$HNO_3\text{, aq.} + \text{KOH, aq.} = KNO_3\text{, aq.} + H_2O + 13.77 \text{ Cal.,}$$
$$\text{HCl, aq.} + \text{LiOH, aq.} = \text{LiCl, aq.} + H_2O + 13.70 \text{ Cal.}$$

Here again it would be difficult to explain the phenomenon without the theory of electrolytic dissociation. In terms of this theory, however, the explanation is perfectly plausible. If MOH and HA represent any strong base and any strong acid respectively, then when equivalent amounts of these are dissolved in water, each solution being largely diluted to the same volume, the reaction may be written thus: —

$$M^{\cdot} + OH' + H^{\cdot} + A' = M^{\cdot} + A' + H_2O + 13.7 \text{ Cal.}$$

Disregarding the ions which occur on both sides of the equality sign, we have

$$OH' + H^{\cdot} = H_2O + 13.7 \text{ Cal.}$$

It thus appears that the neutralization of a strong acid by a strong base in dilute solution consists solely in the combination of hydrogen and hydroxyl ions to form undissociated water, the heat of this ionic reaction being 13.7 large calories.

The heat of formation of water from its ions must not be confused with the heat of formation of water from its elements. When weak acids or weak bases are neutralized by strong bases or strong acids, or when weak acids are neutralized by weak bases, the heat of neutralization may differ widely from 13.7 Cal. This is shown by the following thermochemical equations: —

---

* Loc. cit.

$$H\cdot COOH, aq. + NaOH, aq. = H\cdot COONa, aq. + H_2O + 13.40 \text{ Cal.},$$
$$HCl_2\cdot COOH, aq. + NaOH, aq. = HCl_2\cdot COONa, aq. + H_2O + 14.83 \text{ Cal.},$$
$$H\cdot COOH, aq. + NH_4OH, aq. = H\cdot COONH_4, aq. + H_2O + 11.90 \text{ Cal.},$$
$$HCN, aq. + NaOH, aq. = NaCN, aq. + H_2O + 2.90 \text{ Cal.}$$

As will be seen, the heat of neutralization may be either greater or less than 13.7 Cal. The exceptions to the generalization of constant heat of neutralization are readily explained by the theory of electrolytic dissociation. Suppose a weak acid to be neutralized by a strong base. According to the dissociation theory, the acid is only slightly dissociated and, therefore, yields a comparatively small number of hydrogen ions to the solution. The base on the other hand is completely dissociated into hydroxyl and metallic ions. Therefore, as many hydroxyl ions disappear as there are free hydrogen ions with which they can combine to form water. When the equilibrium between the acid and the products of its dissociation has been thus disturbed, it undergoes further dissociation and the resulting hydrogen ions immediately combine with the free hydroxyl ions of the base. This process continues until all of the hydroxyl ions of the base have been neutralized. It is evident that the thermal effect in this case is the algebraic sum of the heat of dissociation of the weak acid, which may be positive or negative, and the heat of formation of water from its ions. A similar explanation holds for the neutralization of a weak base by a strong acid, or for the neutralization of a weak acid by a weak base. This affords a method for estimating the approximate value of the heat of dissociation of a weak acid or a weak base. For example, in the equation given above,

$$HCN, aq. + NaOH, aq. = NaCN, aq. + H_2O + 2.90 \text{ Cal.},$$

the difference between 2.9 and 13.7 or −10.8 Cal. represents approximately the heat of dissociation of hydrocyanic acid.

Since the acid is initially slightly dissociated in dilute solution, it is apparent that in order to obtain the true heat of dissociation, we must add to −10.8 Cal. the thermal value of the dissociation of that portion of the acid which has already become ionized.

Heat of Ionization. Since 13.7 Cal. is the heat of formation of water from its ions, this must also be the thermal equivalent of the energy required to dissociate one mol of water into its ions. It must be remembered that the dissociated molecule of water must be mixed with a very large volume of undissociated water, in order that the dissociation may be permanent. Reference to the table of heats of formation (p. 296), will show that 68.4 Cal. are required to form one mol of water from its elements. Hence, it follows that 68.4 − 13.7 = 54.7 Cal., is the heat of formation of one equivalent of hydrogen and hydroxyl ions. It has been shown that an extremely small amount of energy is necessary to ionize hydrogen when it is dissolved in water. It is evident, therefore, that 54.7 Cal. is a close approximation to the heat of formation of one equivalent of hydroxyl ions.

HEAT OF FORMATION OF IONS.

Ion.	Heat of Formation.	Ion.	Heat of Formation.
Hydrogen	0.0	Copper (ic)	−15.8
Potassium	61.9	Copper (ous)	−16.0
Sodium	57.5	Mercury (ous)	−19.8
Lithium	62.9	Silver	−25.3
Ammonium	32.8	Lead	0.5
Magnesium	109.0	Tin (ous)	3.3
Calcium	109.0	Chlorine	39.3
Aluminium	121.0	Bromine	28.2
Manganese	50.2	Iodine	13.1
Iron (ous)	22.2	Sulphate	214.4
Iron (ic)	−9.3	Sulphite	151.3
Cobalt	17.0	Nitrous	27.0
Nickel	16.0	Nitric	49.0
Zinc	35.1	Carbonate	161.1
Cadmium	18.4	Hyroxyl	54.7

On the assumption that the heat of ionization of gaseous hydrogen in solution is zero, the values of the other ionic heats of formation may be computed. For example, the heat of formation of KOH, aq. is 116.5 Cal. The ionic heat of formation of potassium ions must be $116.5 - 54.7 = 61.8$ Cal. In like manner, the heat of formation of KCl, aq. is 101.2 Cal.; hence the ionic heat of formation of chlorine ions must be $101.2 - 61.8 = 39.4$ Cal. The preceding table of ionic heats of formation has been calculated as in the above examples.

The Principle of Maximum Work. A fundamental principle of the science of mechanics is, that a system is in stable equilibrium when its potential energy is a minimum. In 1879, Berthelot * suggested that a similar principle applies to chemical systems.

In terms of the kinetic theory, the temperature of a substance is to be regarded as a measure of the kinetic energy of its molecules. The development of heat by a chemical reaction would, therefore, be taken as an indication of a decrease in the potential energy of the system. Berthelot's theorem, known as the *principle of maximum work*, may be stated as follows: — "*Every chemical process accomplished without the intervention of any external energy tends to produce that substance or system of substances which evolves the maximum amount of heat.*" The table of heats of formation (p. 296), illustrates the general truth of this principle, but as will be seen, the theorem precludes the possibility of spontaneous endothermic reactions. Thus, for example, the formation of acetylene from its elements at the temperature of the electric arc is a well-known endothermic reaction, but according to the principle of maximum work, it could not take place spontaneously. Another serious objection to Berthelot's principle is, that according to it, all chemical reactions should proceed to completion, the reaction taking place in such a way as to evolve the greatest amount of heat. As is well known, many reactions, and theoretically all reactions, are never complete, but proceed until a condition of equilibrium is reached. The principle of maximum work, therefore, denies the existence of equilibria in chemical reactions. Many attempts have been made to "explain away" these defects, but none of them have been successful. In referring to the generalization, Le Chatelier terms it "a very interesting approximation toward a strictly valid generalization."

---

* Essai de Mecanique Chimique.

The Theorem of Le Chatelier. As a result of his attempts to modify the principle of maximum work and render it generally applicable, Le Chatelier was led to the discovery of a rigorous law of wide-reaching usefulness. His generalization may be stated as follows: — *Any alteration in the factors which determine an equilibrium, causes the equilibrium to become displaced in such a way as to oppose, as far as possible, the effect of the alteration.* If the temperature of a system which is in equilibrium be raised or lowered, the resulting displacement of the equilibrium is accompanied by such absorption or evolution of heat as will tend to maintain the temperature constant. An interesting illustration of the behavior of a system when one of the factors controlling the equilibrium is varied, is afforded by the system

$$2\,NO_2 \rightleftarrows N_2O_4.$$

The reaction proceeds in the direction indicated by the upper arrow with the evolution of 12.6 Cal. Increase of temperature favors the reaction which is accompanied by an absorption of heat, which in this case, is the reaction indicated by the lower arrow. Hence as the temperature rises, the percentage of NO_2 increases at the expense of N_2O_4. This fact can be demonstrated by the following experiment. Some liquefied N_2O_4 is placed in each of three long glass tubes, which are sealed at one end. When enough N_2O_4 has vaporized to displace the air, the open ends of the tubes are sealed. Changes in the equilibrium caused by varying the temperature can be followed by noting the changes in the color of the mixture. N_2O_4 is an almost colorless substance, while NO_2 is reddish brown. At ordinary temperatures the contents of the tubes will be brown in color. One tube is set aside as a standard of comparison, while the temperature of the second is lowered by surrounding it with a freezing mixture. As the temperature falls, the brown color of the contents of the tube becomes much lighter, showing an increased formation of N_2O_4. The third tube is heated by immersing it in a beaker of boiling water. As the temperature rises, the contents of the tube becomes much darker in color, indicating an increase in the amount of NO_2 in the mixture.

Another example is afforded by the equilibrium between ozone and oxygen, represented by the equation

$$2\,O_3 \rightleftarrows 3\,O_2.$$

The reaction indicated by the upper arrow is exothermic. Increase of temperature causes a displacement of the equilibrium in the direction of the lower arrow, since under these conditions heat is absorbed. Thus, as the temperature rises ozone becomes increasingly stable. Nernst has calculated that at 6000° C., the temperature of the photosphere of the sun, 10 per cent of the above equilibrium mixture would be ozone. Other applications of the theorem of Le Chatelier will be given in subsequent chapters.

PROBLEMS.

1. From the following data calculate the heat of formation of HNO_2 aq. —

$$[NH_4NO_2] = (N_2) + 2\,H_2O + 71.77 \text{ Cal.},$$
$$2\,(H_2) + (O_2) = 2\,H_2O + 136.72 \text{ Cal.},$$
$$(N_2) + 3\,(H_2) + \text{aq.} = 2\,NH_3 \text{ aq.} + 40.64 \text{ Cal.},$$
$$NH_3 \text{ aq.} + HNO_2 \text{ aq.} = NH_4NO_2 \text{ aq.} + 9.110 \text{ Cal.},$$
$$[NH_4NO_2] + \text{aq.} = NH_4NO_2 \text{ aq.} - 4.75 \text{ Cal.}$$

Ans. $(H) + (N) + (O_2) + \text{aq.} = HNO_2 \text{ aq.} + 30.77$ Cal.

2. By the combustion at constant pressure of 2 grams of hydrogen with oxygen to form liquid water at 17° C., 68.36 Cal. are evolved. What is the heat evolution at constant volume? *Ans.* 67.49 Cal.

3. The heats of solution of Na_2SO_4, $Na_2SO_4.H_2O$, and $Na_2SO_4.10\,H_2O$ are 0.46, − 1.9 and − 18.76 Cal. respectively. What are the heats of hydration of Na_2SO_4; (a) to monohydrate, (b) to decahydrate?
Ans. (a) 2.36 Cal., (b) 19.22 Cal.

4. The heats of neutralization of NaOH and NH_4OH by HCl are 13.68 and 12.27 Cal. respectively. What is the heat of ionization of NH_4OH, if it is assumed to be practically undissociated? *Ans.* 1.41 Cal.

5. From the following energy equations: —

$[C] + (O_2) = (CO_2) + 96.96$ Cal.,
$2\,(H_2) + (O_2) = 2\,H_2O + 136.72$ Cal.,
$2\,C_6H_6 + 15\,(O_2) = 12\,(CO_2) + 6\,H_2O + 1598.7$ Cal.,
$2\,(C_2H_2) + 5\,(O_2) = 4\,(CO_2) + 2\,H_2O + 620.1$ Cal.,

all at 17° C. and constant pressure, calculate the heat evolved at 17° C. in the reaction

$$3\,C_2H_2 = C_6H_6,$$

(a) at constant pressure, and (b) at constant volume.
Ans. (a) 130.8 Cal., (b) 129.07 Cal.

6. Calculate the heat of formation of sulphur trioxide from the following energy equations: —

$[PbO] + [S] + 3\,(O) = [PbSO_4] + 1655$ K.
$[PbO] + H_2SO_4.5\,H_2O = [PbSO_4] + 6\,H_2O + 233$ K.
Combined [illegible] $[S] + 3\,(O) + 6\,H_2O = H_2SO_4.5\,H_2O + 1422$ K.
$[SO_3] + 6\,H_2O = H_2SO_4.5\,H_2O + 411$ K.
Ans. $[S] + 3\,(O) = [SO_3] + 1011$ K.

7. What is the heat of formation of a very dilute solution of calcium chloride? (See table on p. ~~257~~ 296.) *Ans.* 187.6 Cal.

CHAPTER XV.

HOMOGENEOUS EQUILIBRIUM.

Historical Introduction. In this and the two succeeding chapters, the conditions which affect the rate and the extent of chemical reactions will be considered. When two substances react chemically, it is customary to refer the phenomenon to the existence of an attractive force known as chemical affinity.

Ever since the metaphysical speculations of the Greeks, who endowed the atoms with the instincts of love and hate, the nature of chemical affinity has been under discussion. So little has been learned as to the cause of chemical reactions, that in recent years this question has been dismissed and attention has been directed to the more promising question as to how they take place. Newton's discovery of the law of gravitation led him to consider the attraction between atoms and the attraction between large masses of matter as manifestations of the same force.

Although Newton found that chemical attraction does not follow the law of the inverse square, yet his suggestion exerted a profound influence upon the minds of his contemporaries.

Geoffroy and Bergmann arranged chemical substances in the order of their displacing power. Thus, if we have three substances, A, B, and C and the attraction between A and B is greater than that between A and C, then when B is added to AC it will completely displace C, as indicated by the following equation: —

$$AC + B = AB + C.$$

These investigators overlooked a factor of fundamental importance in conditioning chemical reactivity, viz., the influence of mass. The importance of the relative amounts of the reacting substances in determining the course of a reaction was first clearly recognized by Wenzel * in 1777. It remained for Berthollet,† however, to point out the significance of the views advanced by Wenzel. His first paper on this subject was published in 1799, while acting as a scientific adviser to Napoleon on his Egyptian expedition. Under ordinary conditions sodium carbonate and calcium chloride react according to the equation,

---

* Lehre von der chemischen Verwandtschaft der Körper.

† Essai de Statique Chimique.

$$Na_2CO_3 + CaCl_2 = 2\,NaCl + CaCO_3,$$

the reaction proceeding nearly to completion. Berthollet observed the deposits of sodium carbonate on the shores of certain saline lakes in Egypt, and pointed out that this salt is produced by the reversal of the above reaction, the large excess of sodium chloride in solution in the water of the lakes conditioning the course of the reaction.

The German chemist Rose* furnished much additional evidence in favor of the effect of mass on chemical reactions. He pointed out that in nature, the silicates, which are among the most stable compounds known, are undergoing a continual decomposition under the influence of such relatively weak agents as water and carbon dioxide. The relatively strong specific affinities of the atoms of the silicates are overcome by the preponderating masses of water and carbon dioxide in the atmosphere. In 1862 an important contribution to our knowledge of the effect of mass on the course of a chemical reaction was made by Berthelot and Péan de St. Gilles.† They investigated the formation of esters from alcohols and acids. The reaction between ethyl alcohol and acetic acid is represented by the equation

$$C_2H_5OH + CH_3COOH \rightleftarrows CH_3COOC_2H_5 + H_2O.$$

Starting with equivalent quantities of alcohol and acid, the reaction proceeds until about two-thirds of the reacting substances have been converted into ester and water. In like manner, if equivalent quantities of ethyl acetate and water are brought together, the reaction proceeds in the direction indicated by the lower arrow, until about one-third of the original substances have been converted into acid and alcohol. In other words the reaction is reversible, a condition of equilibrium resulting when the speeds of the two reactions, indicated by the upper and lower arrows, become equal. If now a fixed amount of acid is taken, say 1 equivalent, and the quantity of alcohol is varied, a corresponding displacement of the equilibrium follows.

---

* Pogg. Ann., 94, 481 (1855); 95, 96, 284, 426 (1855).

† Ann. Chim. Phys. [3], 65, 385; 66, 5; 68, 225 (1862–1863).

The following table gives the results obtained by Berthelot and Péan de St. Gilles for ethyl alcohol and acetic acid. The first and third columns give the number of equivalents of alcohol to 1 equivalent of acetic acid, and the second and fourth columns give the percentage of ester formed.

Equivalents of Alcohol.	Ester Formed.	Equivalents of Alcohol.	Ester Formed.
0.2	19.3	2.0	82.8
0.5	42.0	4.0	88.2
1.0	66.5	12.0	93.2
1.5	77.9	50.0	100.0

The effect of increasing the mass of alcohol on the course of the reaction is very beautifully shown by the above results.

The Law of Mass Action. While the influence of the relative masses of the reacting substances in conditioning chemical reactions was thus fully established, it was not until 1867 that the law governing the action of mass was accurately formulated.

In that year Guldberg and Waage,* two Scandinavian investigators, enunciated the law of mass action as follows: — *The amount of chemical action at any stage of a reaction is proportional to the active masses of the reacting substances present at that time.* Guldberg and Waage defined the term "active mass" as the molecular concentration of the reacting substances. It is to be carefully noted that the amount of chemical action is not porportional to the actual masses of the substances present, but rather to the amounts present in unit volume. The law is generally applicable to homogeneous systems; that is, to those systems in which ordinary observation fails to reveal the presence of essentially different parts. The amount of chemical action exerted by a substance can be determined, either from its effect on the equilibrium, or from its influence on the speed of reaction.

---

* Etudes sur les Affinités Chimiques, Jour. prakt. Chem. [2], 19, 69 (1879).

In order to apply the law of mass action practically, it must be formulated mathematically. Let a and b denote the molecular concentrations of the substances initially present in a reversible reaction. According to the law of mass action, the rate at which these substances combine is proportional to the active masses of each constituent, and therefore to their product, ab. The initial speed of the reaction at the time t_0 is therefore,

$$\text{Speed}_{t_0} \propto ab, \text{ or } \text{Speed}_{t_0} = k \cdot ab,$$

in which the proportionality factor k, is known as the *velocity constant*. As the reaction proceeds, the molecular concentrations of the original substances steadily diminish, while the molecular concentrations of the products of the reaction steadily increase. Let us assume that after the interval of time t, x equivalents of the products of the reaction have been formed. The speed of the original reaction will now be

$$\text{Speed}_t = k\,(a - x)\,(b - x).$$

As the reaction proceeds, the tendency of the products to combine and reform the original substances increases. At the time t, when the concentration of the products is x, the speed of the reverse reaction will be

$$\text{Speed}_t = k_1 \cdot x^2,$$

where k_1 is the velocity constant of the reverse reaction.

We thus have two reactions proceeding in opposite directions: the speed of the direct reaction continuously diminishes while that of the reverse reaction continually increases. It is evident that a point must ultimately be reached at which the speeds of the direct and reverse reactions become equal, and a condition of equilibrium will be established. Let x_1 represent the value of x when equilibrium is attained; we then have

$$\text{Speed}_{\text{direct}} = k\,(a - x_1)\,(b - x_1) = \text{Speed}_{\text{reverse}} = k_1 x_1^2,$$

or

$$\frac{(a - x_1)\,(b - x_1)}{x_1^2} = \frac{k_1}{k} = K,$$

in which K is known as the *equilibrium constant*. Since the velocity constants k and k_1, are independent of the concentration, it follows that the above equation holds for all concentrations. Therefore, if the value of the equilibrium constant of a reaction is known, the equilibrium conditions can be calculated for any concentrations of the reacting substances. When more than one mol of a substance is involved in a reaction, each mol must be considered separately in the mass action equation.

Thus, let

$$n_1A_1 + n_2A_2 + \ldots \rightleftarrows n_1'A_1' + n_2'A_2' + \ldots$$

represent any reversible reaction, in which n_1 mols of A_1 and n_2 mols of A_2 react to form n_1' mols of A_1' and n_2' mols of A_2'. When equilibrium is attained, we shall have

$$k\,c_{A_1}^{n_1}c_{A_2}^{n_2} \ldots = k_1 c_{A_1'}^{n_1'}c_{A_2'}^{n_2'}, \ldots$$

or

$$\frac{c_{A_1}^{n_1}c_{A_2}^{n_2} \ \ldots}{c_{A_1'}^{n_1'}c_{A_2'}^{n_2'} \ \ldots} = \frac{k_1}{k} = K_c, \qquad (1)$$

in which the symbol c is used to denote the active mass, or molecular concentration of the substances involved in the reaction. This is a perfectly general form of the mass-action equation. Since at any one temperature, concentration and pressure are proportional, we may write equation (1) in the following form

$$\frac{p_{A_1}^{n_1}p_{A_2}^{n_2} \ \ldots}{p_{A_1'}^{n_1'}p_{A_2'}^{n_2'} \ \ldots} = K_p, \qquad (2)$$

which, in the case of gaseous equilibria, is often a more convenient form of the equation.

The relation between the two equilibrium constants, K_c and K_p, can be easily determined, as follows: — Since $c = \frac{1}{v} = \frac{p}{RT}$ we have, on substituting this value of c in equation (1),

$$\frac{\left(\frac{p_{A_1}}{RT}\right)^{n_1}\left(\frac{p_{A_2}}{RT}\right)^{n_2} \ \ldots}{\left(\frac{p_{A_1'}}{RT}\right)^{n_1'}\left(\frac{p_{A_2'}}{RT}\right)^{n_2'} \ \ldots} = (RT)^{(n_1'+n_2')-(n_1+n_2)}\,K_p,$$

or indicating the sum of the initial number of mols by Σn and the sum of the final number of mols by $\Sigma n'$, we have

$$K_c = K_p\,(RT)^{\Sigma n' - \Sigma n}.$$

It is evident, therefore, that in reactions where the same number of mols occur on both sides of the equality sign, $K_c = K_p$. Equation (1) (or equation (2)) is sometimes known as the *reaction isotherm*. While the law of mass action may be proved thermodynamically, a much simpler kinetic derivation has been given by van't Hoff. If we assume that the rate of chemical change is proportional to the number of collisions per unit of time between the molecules of the reacting substances, then in the reaction

$$n_1A_1 + n_2A_2 + \ldots = n_1'A_1' + n_2'A_2' + \ldots,$$

the velocity of the direct change will be $kc_{A_1}^{n_1}c_{A_2}^{n_2} \ldots$ and the velocity of the reverse reaction will be $k_1c_{A_1'}^{n_1'}c_{A_2'}^{n_2'} \ldots$

At equilibrium, the two velocities will be equal and, therefore,

$$kc_{A_1}^{n_1}c_{A_2}^{n_2} \ldots = k_1c_{A_1'}^{n_1'}c_{A_2'}^{n_2'} \ldots$$

or

$$\frac{c_{A_1}^{n_1}c_{A_2}^{n_2} \ldots}{c_{A_1'}^{n_1'}c_{A_2'}^{n_2'} \ldots} = \frac{k_1}{k} = K.$$

As a consequence of the assumptions involved in both the thermodynamic and the kinetic proofs of the law of mass action, it follows that the law is only strictly applicable to very dilute solutions. Notwithstanding this limitation, experimental results indicate that it frequently holds for moderately-concentrated solutions.

Equilibrium in Homogeneous Gaseous Systems.

(a) *Decomposition of Hydriodic Acid.* A typical example of equilibrium in a gaseous system is afforded by the decomposition of hydriodic acid, as represented by the equation

$$H_2 + I_2 \rightleftarrows 2\,HI.$$

This reaction has been thoroughly investigated by Hautefeuille, Lemoine and Bodenstein.* The reaction is well adapted for investigation since it proceeds very slowly at ordinary temperatures, while at the temperature of boiling sulphur, 448° C., equilibrium is established quite rapidly. If the mixture of gases is maintained at 448° C. for some time and is then cooled quickly, the respective concentrations of the components of the mixture can be determined by the ordinary methods of chemical analysis. Various mixtures of the gases are sealed in glass tubes and heated for a definite time in the vapor of boiling sulphur. The tubes are then cooled rapidly to the temperature of the room and, after the iodine and hydriodic acid have been removed by absorption in potassium hydroxide, the amount of free hydrogen present in each tube is measured.

---

* Zeit. Phys. Chem. **22**, 1 (1897).

Applying the law of mass action to the above equation, we have

$$\frac{c_{H_2} \cdot c_{I_2}}{c^2_{HI}} = K_c.$$

Expressing the analytical results in mols, let a mols of iodine be mixed with b mols of hydrogen, and let $2x$ mols of hydriodic acid be formed. Then when equilibrium is established, $a - x$ will be the amount of iodine vapor and $b - x$ will be the amount of hydrogen present. The concentrations being directly proportional to the amounts present, we may substitute these values for c_{H_2}, c_{I_2}, and c_{HI} in the mass-action equation. The following expression is thus obtained: —

$$\frac{(b - x)(a - x)}{4x^2} = K_c.$$

Solving the equation for x, we obtain

$$2x = \frac{a + b - \sqrt{a^2 + b^2 - ab\,(2 - 16K_c)}}{1 - 4K_c}.$$

Since, according to Avogadro's law, equal volumes of all gases contain the same number of molecules, volumes may be substituted for a, b, and x. Bodenstein expressed his results in terms of volumes reduced to standard conditions of temperature and pressure. On analyzing equilibrium mixtures, Bodenstein found that at 448° C., $K_c = 0.01984$, and at 350° C., $K_c = 0.01494$.

Having determined the value of the equilibrium constant, he made use of this value in calculating the volume of hydriodic acid which should be obtained from known volumes of hydrogen and iodine. A comparison of the calculated and observed values showed excellent agreement. The following table contains a few of the results obtained by Bodenstein at 448° C.

Hydrogen, b.	Iodine, a.	HI calculated, $2x$.	HI observed, $2x$.
20.57	5.22	10.19	10.22
20.60	14.45	25.54	25.72
15.75	11.90	20.65	20.70
14.47	38.93	27.77	27.64
8.10	2.94	5.64	5.66
8.07	9.27	13.47	13.34

It is of interest to note that a change in pressure does not alter the equilibrium in this gaseous system. Making use of the partial pressures of the components of the gaseous system instead of the concentrations, we have

$$\frac{p_{H_2} \cdot p_{I_2}}{p^2_{HI}} = K_p.$$

Now let the total pressure on the system be increased to n times its original value; then the partial pressures are all increased in the same proportion, and we have

$$\frac{np_{H_2} \cdot np_{I_2}}{n^2p^2_{HI}} = K_p,$$

which is equivalent to the original expression, since n cancels out. The equilibrium is thus seen to be independent of the pressure. This is only true for those systems in which a change in volume does not occur.

(b) *Dissociation of Phosphorus Pentachloride.* When phosphorus pentachloride is vaporized it dissociates according to the following equation

$$PCl_5 \rightleftarrows PCl_3 + Cl_2.$$

Applying the law of mass action, we have

$$\frac{c_{PCl_3} \cdot c_{Cl_2}}{c_{PCl_5}} = K_c.$$

Starting with 1 mol of phosphorus pentachloride, which if undissociated would occupy the volume V', under atmospheric pressure, and letting α denote the degree of dissociation, the molecular concentrations at equilibrium will be as follows: —

$$c_{PCl_5} = \frac{1-\alpha}{(1+\alpha)\,V'}, \quad c_{PCl_3} = \frac{\alpha}{(1+\alpha)\,V'}, \text{ and } c_{Cl_2} = \frac{\alpha}{(1+\alpha)\,V'}.$$

Letting $(1+\alpha)\,V' = V$, and substituting in the above equation, we have

$$\frac{\frac{\alpha}{V} \times \frac{\alpha}{V}}{\frac{1-\alpha}{V}} = \frac{\alpha^2}{(1-\alpha)\,V} = K_c.$$

At 250° C. phosphorus pentachloride is dissociated to the extent of 80 per cent. Under atmospheric pressure 1 mol will be present in $22.4\frac{273+250}{273}$ liters $= V'$. The final volume will, therefore, be

$$V = (1+0.8)\left(22.4\frac{273+250}{273}\right).$$

The value of the equilibrium constant, — usually designated in cases of dissociation, the *dissociation constant*, — is, therefore,

$$K_c = \frac{(0.8)^2}{(1-0.8)\,(1+0.8)\left(22.4\frac{273+250}{273}\right)}.$$

Having obtained the value of K_c, the direction and extent of the reaction at 250° C. can be determined, provided the initial molecular concentrations are known. The reaction is accompanied by a change in volume, and, therefore, the equilibrium is displaced by a change in pressure. Making use of the partial pressures of the components of the gaseous mixture, we have

$$\frac{p_2^2}{p_1} = K_p,$$

where p_1 and p_2 are the partial pressures of phosphorus pentachloride and the products of the dissociation, phosphorus trichloride and chlorine, respectively. Let the total pressure be increased n-times, then

$$K_p = \frac{n^2 p_2^2}{n p_1} = \frac{n p_2^2}{p_1}.$$

It is apparent from this equation, that the equilibrium is not independent of the pressure, an increase in pressure being accompanied by a diminution of the dissociation. An important point in connection with dissociation, first observed by Deville,* is the effect on the equilibrium of the addition of an excess of one of the products of dissociation. For example, in the equilibrium

$$PCl_5 \rightleftarrows PCl_3 + Cl_2,$$

an excess of chlorine or of phosphorus trichloride, drives back the dissociation. If p_1 denotes the partial pressure of phosphorus pentachloride, p_2 that of phosphorus trichloride, and p_3 that of chlorine, then we have

$$\frac{p_2 \cdot p_3}{p_1} = K_p.$$

Now let an excess of chlorine be added; this will cause the value of p_3 to increase. Since the value of K_p is constant, the value of p_2 must diminish and that of p_1 must increase. Hence, the addition of an excess of either product of dissociation causes a diminution of the amount of the dissociation.

(c) *Dissociation of Carbon Dioxide.* Carbon dioxide dissociates according to the equation,

$$2\,CO_2 \rightleftarrows 2\,CO + O_2.$$

This is a somewhat more complex gaseous system than either of the foregoing systems. When equilibrium is established, let p_1 be the partial pressure of the carbon dioxide, p_2 the partial pressure of carbon monoxide, and p_3 the partial pressure of oxygen, then we have

$$\frac{p_2^2 \cdot p_3}{p_1^2} = K_p.$$

At 3000° C. and under atmospheric pressure, carbon dioxide is

---

* Leçons sur la dissociation, Paris (1866).

40 per cent dissociated. The partial pressures of each of the components may be readily calculated as follows: —

$$p_1 = \frac{2\,(1 - 0.40)}{2\,(1 - 0.40) + 3 \times 0.40} = 0.50,$$

$$p_2 = \frac{2 \times 0.40}{2\,(1 - 0.40) + 3 \times 0.40} = 0.33,$$

$$p_3 = \frac{0.40}{2\,(1 - 0.40) + 3 \times 0.40} = 0.17.$$

Substituting these values in the above equation, we obtain

$$K_p = \frac{(0.33)^2 \times 0.17}{(0.50)^2} = 0.074.$$

The dissociation constant for carbon dioxide may have a different value if the equation is written in the form

$$CO_2 \rightleftarrows CO + \tfrac{1}{2}\,O_2.$$

Applying the law of mass action, we have

$$K_p = \frac{p_3\sqrt{p_2}}{p_1}.$$

Substituting the above values of the partial pressures, we obtain

$$K_p = 0.272.$$

Equilibrium in Liquid Systems. The reaction between an alcohol and an acid to form an ester and water may be taken as an example of equilibrium in a liquid system. In the reaction

$$C_2H_5OH + CH_3COOH \rightleftarrows CH_3COOC_2H_5 + H_2O,$$

let a, b, and c represent the number of mols of alcohol, acid and water respectively, which are present in V liters of the mixture, and let x denote the number of mols of ester and water which have been formed when the system has reached equilibrium.

The active masses of the components will then be,

$$C_{\text{alc.}} = \frac{a - x}{V},\quad C_{\text{acid}} = \frac{b - x}{V};\quad C_{\text{ester}} = \frac{x}{V};\ \text{and}\quad C_{\text{water}} = \frac{c + x}{V}.$$

Applying the law of mass action, we obtain

$$\frac{(a - x)\,(b - x)}{x\,(c + x)} = K_c.$$

In this case the value of the equilibrium constant is independent of the volume. This reaction has been studied, as already mentioned, by Berthelot and Péan de St. Gilles.* They found that when equivalent amounts of alcohol and acid are mixed, the reaction proceeds until two-thirds of the mixture is changed into ester and water. Hence, we find

$$K_c = \frac{\frac{1}{3} \times \frac{1}{3}}{\frac{2}{3} \times \frac{2}{3}} = \tfrac{1}{4}.$$

Having determined the value of K_c, it may now be used to calculate the equilibrium conditions for any initial concentrations of the substances involved in the reaction. As an illustration, we will take 1 mol of acetic acid and treat it with varying amounts of alcohol, the initial mixture containing neither of the products of the reaction. The equation takes the form

$$\frac{(a - x)(1 - x)}{x^2} = \frac{1}{4}.$$

Solving for x, we have

$$x = \tfrac{2}{3}(1 + a - \sqrt{a^2 - a + 1}).$$

A comparison of the observed and calculated values given in the accompanying table shows that the agreement is excellent, even in the more concentrated solutions, where we might reasonably expect that the mass law would cease to hold.

Alcohol, a.	Ester (observed), x.	Ester (calculated), x.
0.05	0.05	0.049
0.08	0.078	0.078
0.18	0.171	0.171
0.28	0.226	0.232
0.33	0.293	0.311
0.50	0.414	0.523
0.67	0.519	0.528
1.0	0.665	0.667
1.5	0.819	0.785
2.0	0.858	0.845
2.24	0.876	0.864
8.0	0.966	0.945

---

* Loc. cit.

The Variation of the Equilibrium Constant with Temperature. Van't Hoff showed that the displacement of equilibrium due to change in temperature is connected with the heat evolved or absorbed in a chemical reaction by the equations

$$\frac{d\,(\log_e K_c)}{dT} = \frac{Q_v}{RT^2}, \tag{1}$$

and

$$\frac{d\,(\log_e K_p)}{dT} = \frac{Q_p}{RT^2}, \tag{2}$$

where Q_v and Q_p are the heats of reaction at constant volume and constant pressure respectively, and where R and T have their usual significance. Equation (1) is known as the *reaction isochore.* Both equations show that the rate of change of the natural logarithm of the equilibrium constant with temperature is equal to the total heat of reaction divided by the molecular gas constant times the square of the absolute temperature at which the reaction takes place. Equations (1) and (2) hold only for displacements of the equilibrium due to infinitely small changes in temperature. In order to render these equations applicable to concrete equilibria, it is necessary to integrate them. The integration of these expressions can only be performed if Q is constant. For small intervals of temperature, Q is practically independent of the temperature, and for larger intervals we may take the value of Q which corresponds to the mean of the two temperatures between which the integration is performed. Integrating equations (1) and (2) on this assumption, we obtain

$$\log_e K_{c_2} - \log_e K_{c_1} = \frac{Q_v}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right), \tag{3}$$

and

$$\log_e K_{p_2} - \log_e K_{p_1} = \frac{Q_p}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right). \tag{4}$$

Passing to Briggsian logarithms, and putting $R = 1.99$ calories, equations (3) and (4) become

$$\log K_{c_2} - \log K_{c_1} = \frac{Q_v}{4.581}\left(\frac{T_2 - T_1}{T_1 T_2}\right), \tag{5}$$

and

$$\log K_{p_2} - \log K_{p_1} = \frac{Q_p}{4.581}\left(\frac{T_2 - T_1}{T_1 T_2}\right). \qquad (6)$$

We shall now proceed to show how these important equations may be applied to several typical equilibria.

(a) *Vaporization of Water.* The equilibrium between a liquid and its vapor is conditioned by the pressure of the vapor, this in turn being dependent upon the temperature. In this case of physical equilibrium, we have $K_{p_1} = p_1$, and $K_{p_2} = p_2$. The value of Q_p for water can be calculated from the following data: —

$$T_1 = 273^\circ, \qquad p_1 = 4.54 \text{ mm. of mercury,}$$
$$T_2 = 273^\circ + 11^\circ.54, \quad p_2 = 10.02 \text{ mm. of mercury.}$$

Substituting in equation (6), we have

$$Q_p = \frac{4.581\,(\log 10.02 - \log 4.54)\,273 \times 284.5}{273 - 284.5},$$

or $$Q_p = -10{,}670 \text{ calories.}$$

The value of Q_p obtained by experiment is $-10{,}854$ calories.

(b) *Dissociation of Nitrogen Tetroxide.* In the reaction

$$N_2O_4 \rightleftarrows 2\,NO_2,$$

the following values for the dissociation of N_2O_4 have been obtained: —

$$T_1 = 273^\circ + 26^\circ.1, \qquad \alpha_1 = 0.1986,$$
$$T_2 = 273^\circ + 111^\circ.3, \qquad \alpha_2 = 0.9267.$$

If the dissociation takes place under a pressure of 1 atmosphere, then the partial pressures of the component gases will be

$$p_{N_2O_4} = \frac{1-\alpha}{1-\alpha+2\,\alpha}, \text{ and } p_{NO_2} = \frac{2\,\alpha}{1-\alpha+2\,\alpha}.$$

The values of K_{p_1} and K_{p_2} are, then, according to the law of mass action as follows: —

$$K_{p_1} = \frac{\left(\dfrac{2\,\alpha_1}{1+\alpha_1}\right)^2}{\dfrac{1-\alpha_1}{1+\alpha_1}} = \frac{4\,\alpha_1^2}{1-\alpha_1^2},$$

and

$$K_{p_2} = \frac{\left(\frac{2\,\alpha_2}{1+\alpha_2}\right)^2}{\frac{1-\alpha_2}{1+\alpha_2}} = \frac{4\,\alpha_2^2}{1-\alpha_2^2}.$$

Substituting in equation (6) and solving for Q_p, we obtain

$$Q_p = \frac{4.581 \log \frac{4 \times (0.9267)^2}{1-(0.9267)^2} - \log \frac{4 \times (0.1986)^2}{1-(0.1986)^2}\, 299.1 \times 384.3}{299.1 - 384.3},$$

or

$$Q_p = -12{,}260 \text{ calories per mol of } N_2O_4.$$

In a reaction which is accompanied by no thermal change, $Q = 0$, and the right-hand side of equations (1) and (2) becomes equal to zero. In other words, in such a reaction a change in temperature does not cause a displacement of the equilibrium.

The reaction,

$$C_2H_5OH + CH_3COOH \rightleftarrows CH_3COO.C_2H_5 + H_2O,$$

is accompanied by such a small thermal change that it may be considered as zero, and according to the above reasoning there should be only a very slight displacement of the equilibrium when the temperature is varied. Berthelot found that at 10° C., 65.2 per cent of the alcohol and acid are changed into ester, and at 220° C., 66.5 per cent of the mixture is transformed into ester. As will be seen, an increase of 210° produces hardly any displacement of the equilibrium.

PROBLEMS.

1. When 2.94 mols of iodine and 8.10 mols of hydrogen are heated at constant volume at 444° C. until equilibrium is established, 5.64 mols of hydriodic acid are formed. If we start with 5.30 mols of iodine and 7.94 mols of hydrogen, how much hydriodic acid is present at equilibrium at the same temperature? *Ans.* 9.49 mols.

2. At 2000° C., and under atmospheric pressure, carbon dioxide is 1.80 per cent dissociated according to the equation

$$2\,CO_2 \rightleftarrows 2\,CO + O_2.$$

Calculate the equilibrium constant for the above reaction using partial pressures. *Ans.* 3×10^{-6}.

3. What is the equilibrium constant in the preceding problem, if the concentrations are expressed in mols per liter? *Ans.* 1.61×10^{-8}.

4. When 6.63 mols of amylene and 1 mol of acetic acid are mixed, 0.838 mol of ester is formed in the total volume of 894 liters. How much ester will be formed when we start with 4.48 mols of amylene and 1 mol of acetic acid in the volume of 683 liters? *Ans.* 0.8111 mol.

5. If 1 mol of acetic acid and 1 mol of ethyl alcohol are mixed, the reaction

$$C_2H_5OH + CH_3COOH \rightleftarrows CH_3COOC_2H_5 + H_2O,$$

proceeds until equilibrium is reached, when $\frac{1}{3}$ mol of ethyl alcohol, $\frac{1}{3}$ mol of acetic acid, $\frac{2}{3}$ mol of ethyl acetate, and $\frac{2}{3}$ mol of water are present. If we start (a) with 1 mol of acid and 2 mols of alcohol; (b) with 1 mol of acid, 1 mol of alcohol, and 1 mol of water; (c) with 1 mol of ester and 3 mols of water, how much ester will be present in each case at equilibrium?

Ans. (a) 0.845 mol, (b) 0.543 mol, (c) 0.465 mol.

6. In the reaction

$$HCl + \tfrac{1}{2}O \rightleftarrows \tfrac{1}{2}H_2O + Cl,$$

we find, since $\frac{1}{2}O = \frac{1}{4}O_2$, for

$$K_p = \frac{\sqrt{p_{H_2O}} \cdot \sqrt{p_{Cl}}}{p_{HCl} \cdot \sqrt[4]{p_O}},$$

the values 3.02 at 386° C. and 2.35 at 419° C. Calculate the heat evolved by the reaction under constant pressure. *Ans.* 6827 cal.

7. Above 150° C. NO_2 begins to dissociate according to the equation

$$NO_2 \rightleftarrows NO + \tfrac{1}{2}O_2.$$

At 390° C. the vapor density of NO_2 is 19.57 (H = 1), and at 490° C it is 18.04. Calculate the degree of dissociation according to the above equation at each of these temperatures; the equilibrium constants expressing the concentrations in mols per liter; and the heat of dissociation of NO_2.

Ans. $\alpha_1 = 0.35$, $\alpha_2 = 0.55$. $K_1 = 2.884 \times 10^{-2}$.
$K_2 = 7.173 \times 10^{-2}$. $Q = -9407$ cal.

CHAPTER XVI.

HETEROGENEOUS EQUILIBRIUM.

Heterogeneous Systems. We have now to consider equilibria in systems made up of matter in different states of aggregation. Such systems are termed *heterogeneous systems,* as distinguished from those dealt with in the preceding chapter where the composition is uniform throughout. The physically distinct portions of matter involved in a heterogeneous system are known as *phases,* each phase being homogeneous and separated from the other phases by definite bounding surfaces. Thus, ice, liquid water and vapor constitute a physically heterogeneous system. Another heterogeneous system is formed by calcium carbonate and its dissociation products, calcium oxide and carbon dioxide. The equilibrium between a solid, its saturated solution, and vapor affords an illustration of a still more complex heterogeneous system.

Application of the Law of Mass Action to Heterogeneous Equilibria. It has been shown in the preceding chapter that the law of mass action may be applied to homogeneous equilibria provided the molecular condition of the reacting substances is known.

When we attempt to apply the law of mass action to heterogeneous equilibria, especially where solids are involved, the problem presents difficulties. In his investigation of the dissociation of calcium carbonate, according to the equation

$$[CaCO_3] \rightleftarrows [CaO] + (CO_2),$$

Debray * showed that just as every liquid has a definite vapor pressure corresponding to a certain temperature, so there is a definite pressure of carbon dioxide over calcium carbonate at a definite temperature. Furthermore, the pressure was found to be independent of the amount of calcium carbonate present.

---

* Compt. rend., 64, 603 (1867).

Guldberg and Waage * showed that the law of mass action can be applied to such heterogeneous equilibria, provided that the active masses of the solids present are considered as constant.

Nernst pointed out that this statement of Guldberg and Waage can be easily reconciled with experimental facts. In a heterogeneous equilibrium involving solids, it is only necessary to consider the gaseous phase, the active mass of a solid being equivalent to its concentration in the gaseous phase. That is, every solid is to be looked upon as possessing, at a definite temperature, a definite vapor pressure which is entirely independent of the amount of solid present. Such substances as arsenic, antimony, and cadmium are known to have appreciable vapor pressures at relatively low temperatures, and it is quite reasonable to suppose that every solid substance exerts a definite vapor pressure at a definite temperature, even though we have no method sufficiently refined to measure such minute pressures.

Since the active mass of a solid remains constant so long as any of it is present, the application of the law of mass action to certain heterogeneous equilibria is, in general, simpler than its application to homogeneous systems. The truth of this statement will be evident after a few typical heterogeneous systems have been considered.

(a) *Dissociation of Calcium Carbonate.* In the reaction

$$[CaCO_3] \rightleftarrows [CaO] + (CO_2),$$

let π_1 and π_2 represent the pressures due to the vapor of calcium carbonate and calcium oxide respectively, and let p denote the pressure of the carbon dioxide. Applying the law of mass action, we obtain

$$\frac{\pi_2 p}{\pi_1} = K_p.$$

But since π_1 amd π_2 are constant at any one temperature, the equation becomes

$$p = K_p',$$

or, the equilibrium constant at any one temperature is solely dependent upon the pressure of the carbon dioxide evolved. The accompanying table gives the values of the pressure of carbon dioxide corresponding to various temperatures.

---

* Loc. cit.

Temperature, Degrees.	Pressure in Millimeters of Mercury.
547	27
610	46
625	56
740	255
745	289
810	678
812	753
865	1333

(b) *Dissociation of Ammonium Hydrosulphide.* When solid ammonium hydrosulphide is heated, it is almost completely dissociated into ammonia and hydrogen sulphide as shown by the following equation: —

$$[NH_4HS] \rightleftarrows (NH_3) + (H_2S).$$

This reaction was investigated by Isambert,* who found that the total gas pressure at 25°.1 C. is equal to 501 mm. of mercury. Since the partial pressures of the ammonia and hydrogen sulphide are necessarily the same, each must be approximately equal to 250.5 mm., the relatively small pressure due to the undissociated vapor of the ammonium hydrosulphide being neglected. Let π be the partial pressure of the vapor of ammonium hydrosulphide, and let p_1 and p_2 be the partial pressures of the ammonia and hydrogen sulphide. Applying the law of mass action, we have

$$\frac{p_1 \cdot p_2}{\pi} = K_p. \qquad (1)$$

Since π is constant at any one temperature, equation (1) becomes

$$p_1 \cdot p_2 = K_p'.$$

According to Dalton's law of partial pressures, we have

$$P = p_1 + p_2 + \pi,$$

---

* Compt. rend., 93, 595, 730 (1881).

where P is the total pressure. Neglecting the relatively small pressure π, we may write

$$P = p_1 + p_2.$$

Hence, since $p_1 = p_2$,

$$\frac{P}{2} = p_1 = p_2 \cdot$$

Substituting these values in equation (1), we obtain

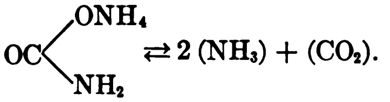
$$\frac{P^2}{4} = K_p' = \frac{(501)^2}{4} = 62{,}750 \cdot$$

The value of the equilibrium constant may be checked by observing the effect on the system of the addition of an excess of either one of the products of the dissociation. The accompanying table gives the results of a few of Isambert's experiments.

Pressure of Ammonia.	Pressure of Hydrogen Sulphide.	$p_{NH_3} \cdot p_{H_2S} = K_p'$.
208	294	61,152
138	458	63,204
417	146	60,882
453	143	64,779
		Mean 62,504

As will be seen, the mean value of the equilibrium constant agrees well with the value found for equivalent amounts of the products of dissociation.

(c) *Dissociation of Ammonium Carbamate.* The dissociation of ammonium carbamate takes place according to the equation



$$OC\begin{cases}ONH_4\\NH_2\end{cases} \rightleftarrows 2\,(NH_3) + (CO_2).$$

This dissociation has been investigated by Horstmann.* Applying the law of mass action, we have

$$\frac{p_1^2 \cdot p_2}{\pi} = K_p, \qquad (2)$$

---

* Lieb. Ann., 187, 48 (1877).

where p_1 and p_2 are the partial pressures of ammonia and carbon dioxide respectively, and where π is the partial pressure of ammonium carbamate. Since π is constant, equation (2) becomes

$$p_1^2 p_2 = K_p'.$$

If P denotes the total gaseous pressure, and π is neglected as in the preceding example, we have, since three mols of gas are formed

$$p_1^2 = \frac{4\,P^2}{9}, \quad \text{and} \quad p_2 = \frac{P}{3}.$$

Substituting these values in equation (2), we have

$$\frac{4\,P^3}{27} = Kp'.$$

This equation has also been tested by Isambert * by adding an excess of ammonia or carbon dioxide to the dissociating system. He found that the value of the equilibrium constant remains practically constant. The addition of a foreign gas was shown to be without effect on the dissociation.

(d) *Dissociation of the Hydrates of Copper Sulphate.* Many interesting examples of heterogeneous equilibrium are furnished by hydrated salts. Thus, if crystallized copper sulphate, $CuSO_4.5\ H_2O$, is placed in a desiccator, it gradually loses water of crystallization and ultimately only the anhydrous salt remains. If the desiccator be provided with a manometer and is so arranged that the temperature can be maintained constant, it is possible to observe the changes in vapor pressure accompanying the process of dehydration. At the temperature of 50° C., the pressure over completely hydrated copper sulphate is found to remain constant at 47 mm. until the salt has been deprived of two molecules of water, when it drops abruptly to 30 mm. and remains constant until two more molecules of water have been lost. It then drops again to 4.4 mm. and remains constant until dehydration is complete.

The successive stages of the dehydration are shown in the accompanying diagram, Fig. 76. The constant pressures observed in the dehydration correspond to the successive equilibria involved.

---

* Loc. cit.

At 50° C. the pentahydrate and the trihydrate are in equilibrium, a pressure of 47 mm. being maintained so long as any of the pentahydrate is present. When all of the pentahydrate is used up, then the trihydrate begins to undergo dehydration into the monohydrate. This is a new equilibrium and the pressure of the aqueous vapor necessarily changes, and remains constant so long as any trihydrate remains. The last stage corresponds to the equilibrium between the monohydrate and the anhydrous salt. The following equations represent the three successive equilibria:—

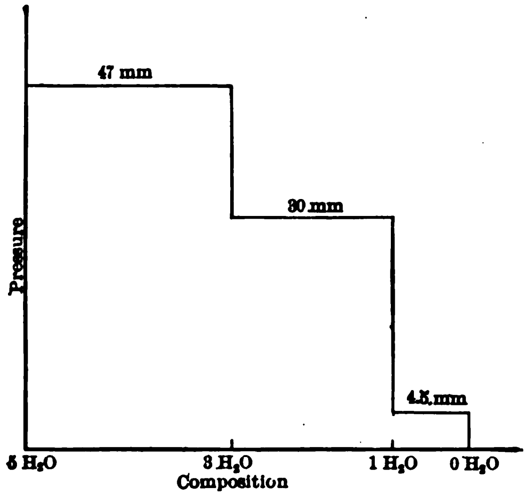


Fig. 76.

(1) $CuSO_4 \cdot 5\,H_2O \rightleftarrows CuSO_4 \cdot 3\,H_2O + 2\,H_2O$,

(2) $CuSO_4 \cdot 3\,H_2O \rightleftarrows CuSO_4 \cdot H_2O + 2\,H_2O$,

(3) $CuSO_4 \cdot H_2O \rightleftarrows CuSO_4 + H_2O$.

Applying the law of mass action to the first of the above equilibria, we have

$$\frac{\pi_2 p^2}{\pi_1} = Kp,$$

in which π_1 and π_2 denote the partial pressures due to the hydrates $CuSO_4.5\,H_2O$ and $CuSO_4.3\,H_2O$ respectively, and p denotes the pressure of aqueous vapor. Since π_1 and π_2 are constant, above expression simplifies to the following

$$p^2 = K_p'.$$

In a similar manner it may be shown that the pressure of aqu vapor in the other equilibria must be constant. It must clearly understood that the observed pressure is only defi and fixed when two hydrates are present. If the dehydra

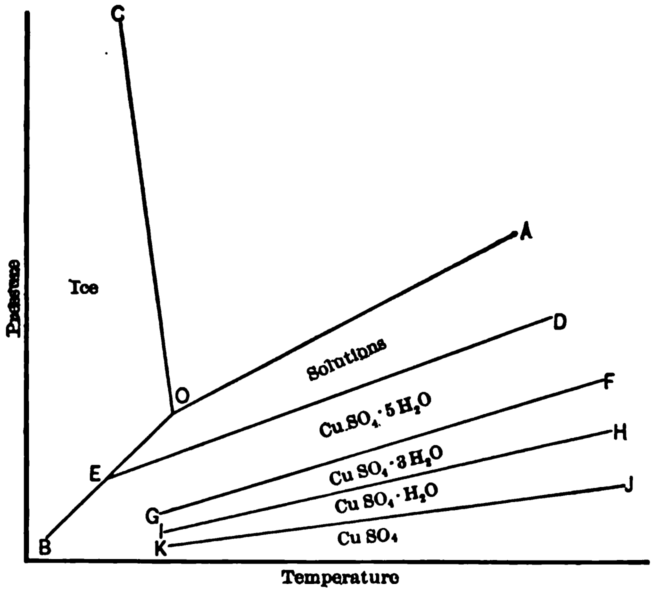


Fig. 77.

were conducted at another temperature than 50° C. the equilib pressure would be different. The vapor pressure curves of different hydrates are shown in the temperature-pressure dia of Fig. 77.

Heat of Dissociation of Solids. When the products of dissociation of a solid are gaseous, it has been pointed out b Forcrand * that the ratio of the heat of dissociation of 1 m solid to the absolute temperature at which the dissociation pressure is equal to 1 atmosphere, is constant. Or, denoting the heat of dissociation by Q and the absolute temperature by T, De Forcrand's relation may be expressed thus,

---

* Ann. Chim. Phys. [7], 28, 545.

$$\frac{Q}{T} = \text{constant} = 33.$$

Nernst has shown that the value of the constant in this relation is not independent of the temperature. Thus, the value of the ratio at 100° C. is 29.7, while at 1000° C. it is 37.7. Up to the present time no expression has been derived in which the variation of the ratio with the temperature is included.

Distribution of a Solute between Two Immiscible Solvents. When an aqueous solution of succinic acid is shaken with ether, the acid distributes itself between the ether and the water in such a way that the ratio between the two concentrations is always constant. It will be seen that the distribution of the succinic acid between the two solvents is analogous to that of a substance between the liquid and gaseous phases (see page 170), and therefore the laws governing the latter equilibrium should apply equally to the former. Nernst * has shown that (a) *If the molecular weight of the solute is the same in both solvents, the ratio in which it distributes itself between them is constant at constant temperature,* or in other words, Henry's law is applicable; and (b) *If there are several solutes in solution the distribution of each solute is the same as if it were present alone.* This is clearly Dalton's law of partial pressures. The ratio in which the solute distributes itself between the two solvents is termed the *coefficient of distribution or partition.* The following table gives the results of three experiments on the distribution of succinic acid between ether and water.

Concentration in Water.	Concentration in Ether.	Distribution Coefficient.
43.4	7.1	6.1
43.8	7.4	5.9
47.4	7.9	6.0

---

* Zeit. phys. Chem., 8, 110 (1891).

As will be seen the distribution coefficient is constant, showing that Henry's law applies. When the molecular weight of a solute is not the same in both solvents the distribution coefficient is not constant, and conversely, if the distribution coefficient is not constant, we infer that the molecular weights of the solute in the two solvents are not identical.

Let us assume that a solute whose normal molecular weight is A, when shaken with two immiscible solvents undergoes polymerization in one of them, its molecular weight being A_n. We then have the equilibrium

$$A_n \rightleftarrows nA:$$

applying the law of mass action, we have

$$\frac{c_A{}^n}{c_{A_n}} = K_c.$$

If the molecular weight in one solvent is twice the molecular weight in the other, then $n = 2$, and

$\frac{c_1{}^2}{c_2}$ or $\frac{c_1}{\sqrt{c_2}}$ = constant, since the two ratios are *not* equal.

Thus Nernst found the following concentrations of benzoic acid when it was shaken with benzene and water.

c_1 (Water).	c_2 (Benzene).	$\frac{c_1}{c_2}$.	$\frac{c_1}{\sqrt{c_2}}$.
0.0150	0.242	0.062	0.0305
0.0195	0.412	0.048	0.0304
0.0289	0.970	0.030	0.0293

As will be seen, the values of the ratio c_1/c_2 steadily decrease, while on the other hand, the values of the ratio $c_1/\sqrt{c_2}$ remain constant. This shows, therefore, that benzoic acid has twice the normal molecular weight in benzene.

The Solution of a Solid in a Non-dissociating Solvent. When a solid is brought in contact with a non-dissociating solvent, it continues to dissolve until the solution becomes saturated. A condition of equilibrium then obtains, the rates of solution and precipitation being the same. This is plainly a case of heterogeneous equilibrium. If c is the concentration of the dissolved substance, and π is the concentration of the undissolved solid, then according to the law of mass action

$$\frac{c}{\pi} = K_c,$$

or since π is constant,

$$c = K_c'.$$

Variation of the Constant of Heterogeneous Equilibrium with Temperature. The reaction isochore equation of van't Hoff

$$\frac{d\,(\log_e K)}{dT} = \frac{Q}{RT^2},$$

which has been shown to connect the displacement of a homogeneous equilibrium with change in temperature, applies equally well to heterogeneous equilibria. The following examples will serve to illustrate its application in such cases.

(a) *Dissociation of Ammonium Hydrosulphide.* In the reaction representing the dissociation of ammonium hydrosulphide,

$$[NH_4HS] \rightleftarrows (NH_3) + (H_2S),$$

let p_1 and p_2 be the partial pressures of ammonia and hydrogen sulphide, and let π be the partial pressure of ammonium hydrosulphide. Then as has been shown (see page 331),

$$K_p' = \frac{P^2}{4},$$

where P is the total gaseous pressure. From the following data:—

$$T_1 = 273° + 9°.5, \qquad P_1 = 175 \text{ mm. of mercury},$$

and

$$T_2 = 273° + 25°.1, \qquad P_2 = 501 \text{ mm. of mercury},$$

we have, on applying the reaction isochore equation, and solving for Q_p,

$$Q_p = \frac{4.581\left[\log\left(\frac{501}{2}\right)^2 - \log\left(\frac{175}{2}\right)^2\right]282.5 \times 298.1}{282.5 - 298.1},$$

or

$$Q_p = -\ 22{,}740 \text{ calories}.$$

This result agrees well with the value, – 22,800 calories, found by direct experiment.

(b) *Solution of Succinic Acid.* The concentration of succinic acid (in a saturated solution) and the temperature, are the factors which determine the equilibrium in this case. In the equation

$$\frac{d\,(\log_e K_c)}{dT} = \frac{Q_c}{RT^2},$$

$K_c = c$, where c is the concentration of succinic acid in a saturated solution. The following experimental data, due to van't Hoff, enables us to calculate the heat of solution of the acid.

$T_1 = 273°$ $\quad c = 2.88$ grams per 100 grams of water,

and

$T_2 = 273° + 8°.5,$ $\quad c = 4.22$ grams per 100 grams of water.

Substituting in the reaction isochore equation and solving for Q_c, we have

$$Q_c = \frac{4.581\,(\log 4.22 - \log 2.88)\,273 \times 281.5}{273 - 281.5},$$

or

$$Q = -\,6871 \text{ calories.}$$

The value of the heat of solution for 1 mol of succinic acid as found by direct experiment is –6700 calories.

The Phase Rule. While it is possible to apply the law of mass action to certain heterogeneous equilibria there are numerous cases where its application is either difficult or impossible. To deal with such heterogeneous systems we make use of a generalization discovered by J. Willard Gibbs,* late professor of mathematical physics in Yale University. This generalization was first stated by Gibbs in 1874, and is commonly known as the phase rule. Before entering upon a discussion of the phase rule, it will be necessary to define a few of the terms employed.

The composition of a system is determined by the number of independent variables or *components* involved. Thus in the system — ice, water, and vapor — there is but a single component. In the system

$$CaCO_3 \rightleftarrows CaO + CO_2,$$

---

* Trans. Connecticut Academy, Vols. II and III, 1875–8.

while there are three constituents of the equilibrium, only two of these need be considered as components, for the amount of any one constituent is not independent of the amounts of the other two, as the following equations show: —

$$CaO + CO_2 = CaCO_3,$$
$$CaCO_3 - CaO = CO_2,$$
$$CaCO_3 - CO_2 = CaO.$$

In general, the components are chosen from the smallest number of independently-variable constituents required to express the composition of each phase entering into the equilibrium, even negative quantities of the components being permissible.

The number of variable factors, — temperature, pressure, and concentration, — of the components which must be arbitrarily fixed in order to define the condition of the system, is known as the *degree of freedom* of the system. For example, a gas has two degrees of freedom since two of the variables, temperature, pressure or volume, must be fixed in order to define it; a liquid and its vapor has only one degree of freedom, since for equilibrium at a certain temperature, there can be but a single pressure; and in a system consisting of a substance in the three states of aggregation, equilibrium can only exist at a single temperature and pressure.

Derivation of the Phase Rule. The following derivation of the phase rule is due to Nernst. Let us assume a complete heterogeneous equilibrium made up of y phases of n components, and let us fix our attention upon one single phase. This phase will contain a certain amount of each one of the n components, the concentrations of which may be designated by $c_1, c_2, c_3, \ldots c_n$. Since we have assumed complete equilibrium to exist, the slightest change in concentration, temperature or pressure will alter the composition of this phase.

This may be expressed by the equation

$$f(c_1, c_2, c_3, \ldots c_n, p, T) = 0,$$

where f is any function of the variables. Since any change in one phase implies a corresponding change in the remaining $y - 1$ phases, it follows that the composition of all the phases is a certain determined function of the same variables.

The above equation is, then, of the form ascribed to each separate phase, and since there are y phases we have y separate equations. There are, however, $n + 2$ variables in each equation, so that if $y = n + 2$, that is if we have two more phases than components, each unknown quantity has a definite known value. In this case there is only one value for c_1, c_2, c_3, c_4, . . . c_n, p and T at which the system can be in equilibrium. Hence when n components are present in $n + 2$ phases, we have equilibrium only for a certain temperature, a certain pressure, and a certain ratio of concentrations of the single phases. That is, $n + 2$ phases of n substances can only exist at a certain point in a co-ordinate system. This point is termed the *transition point*. If one value be altered then one phase vanishes, and there remain $n + 1$ phases of n components, and the problem becomes indeterminate. Thus it is proved that n components are necessary in order that a system containing $n + 1$ phases may exist in complete equilibrium.

The phase rule may be stated as follows: — *A system made up of n components in n + 2 phases can only exist when pressure, temperature and concentration have definite fixed values; a system of n components in n + 1 phases can exist only so long as one of the factors varies; and a system of n components in n phases can exist only so long as two of the factors vary.* If P denotes the number of phases, C the number of components, and F the number of degrees of freedom, then the phase rule may be conveniently summarized by the expression,

$$C - P + 2 = F.$$

Equilibrium in the System, Water, Ice, and Vapor. In this system we may have one, two, or three phases present, according to the conditions. Under ordinary circumstances of temperature and pressure, water and water vapor are in equilibrium. The vapor pressure curve of water is represented by the line OA in the pressure-temperature diagram (Fig. 78). It is only at points on this curve that water and its vapor are in equilibrium. Thus, if the pressure be reduced below that corresponding to any point on OA, all of the water will be vaporized; if on the other hand, the pressure be raised above the curve, all of the vapor will ultimately condense to the liquid state. When the temperature is reduced below 0° C., only ice and vapor are present, the curve OC representing the equilibrium between these two phases. It is to be observed that the curve OC is not continuous with OA. At the point O, where the two curves intersect, ice, water, and water vapor are in equilibrium. At this point ice and water must have the same vapor pressure, otherwise distillation of vapor from the phase having the higher vapor pressure to that with the lower vapor pressure would occur, and eventually the phase having the higher vapor pressure would disappear. This result would be in contradiction to the experimentally-determined fact that both solid and liquid phases are in equilibrium at the point O. The temperature at which ice and water are in equilibrium with their vapor under atmospheric pressure is 0° C. Since increase of pressure lowers the freezing-point of water, the point O, representing the equilibrium between ice and water under the pressure of their own vapor, *viz.*, 4.57 mm., must be a little above 0° C. The exact temperature corresponding to the point O has been found to be 0.°0075 C.

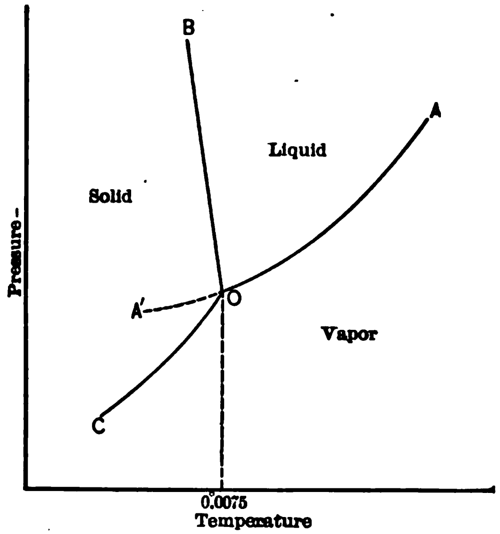


Fig. 78.

The change in the melting-point of ice due to increasing pressure is represented by the line OB. This line is inclined toward the vertical axis because the melting point of ice is lowered by increased pressure. The point O is called a *triple point* because there, and there only, three phases are in equilibrium. As is well known, water does not always freeze exactly at 0° C. If the containing vessel is perfectly clean, and care is taken to exclude dust, it is possible to supercool water several degrees below its freezing-point and measure its vapor pressure.

The dotted curve OA', which is a continuation of OA, represents the vapor pressure of supercooled water. It will be noticed that (1) there is no break in the vapor-pressure curve so long as the solid phase does not separate, and (2) the vapor pressure of supercooled water, which is an unstable phase, is greater than that of ice, the stable phase, at that temperature.

We now proceed to apply the phase rule to this system. In the formula, $C - P + 2 = F$, $C = 1$. It is evident that if $P = 3$, then $F = 0$; or the system has no degree of freedom. We have seen that the triple point O, represents such a condition. At this point ice, water, and water vapor are co-existent, and if either one of the variables, temperature or pressure, is altered, one of the phases disappears; in other words, the system has no degree of freedom. Such a system is said to be *non-variant*. If in the above formula, $P = 2$, then $F = 1$, and the system has one degree of freedom, or is *univariant*. Any point on any one of the curves OA, OB, or OC represents a univariant system. Take, for example, a point on the curve OA. In this case the temperature may be altered without altering the number of phases in equilibrium. If the temperature is raised, a corresponding increase in vapor pressure follows and the system will adjust itself to some other point on the curve OA. In like manner, the pressure may be [illegible] without causing the disappearance of one of the phases. [illegible] the temperature is maintained constant, then a change [illegible] will cause either condensation of water vapor or [illegible] liquid water. Under these conditions the system [illegible] freedom. Again, if $P = 1$, then $F = 2$, [illegible] or has two degrees of freedom. The areas included between the curves in the diagram are examples of bivariant systems. Consider the vapor phase; the temperature may be fixed at any desired value within the vapor area *AOC*, and the pressure may be altered along a line parallel to the vertical axis without causing a change in the number of phases, provided the curves *OA* and *OC* are not intersected.

The System, Sulphur (Rhombic, Monoclinic), Liquid and Vapor. This system is more complicated than the preceding one-component system, since there are two solid phases in addition to the liquid and vapor phases. At ordinary temperatures, rhombic sulphur is the stable modification. When this is heated rapidly it melts at 115° C., but if it is maintained in the neighborhood of 100° C. it gradually changes into monoclinic sulphur which melts at 120° C. Monoclinic sulphur can be kept indefinitely at 100° C. without undergoing change into the rhombic modification, or in other words it is the stable phase at this temperature.

It is evident, therefore, that there must be a temperature above which monoclinic sulphur is the stable form and below which rhombic sulphur is the stable modification. This temperature at which both rhombic and monoclinic modifications are in equilibrium with each other and with their vapor, is termed the *transition point.* Its value has been determined to be 95°.6 C. The change from one form into the other is relatively slow, so that it is possible to measure the vapor pressure of rhombic sulphur up to its melting-point, and that of monoclinic sulphur below its transition point. The vapor pressure of solid sulphur, although very small, has been measured as low as 50° C.

The complete pressure-temperature diagram for sulphur is shown in Fig. 79. At the point *O*, rhombic and monoclinic sulphur are in equilibrium with sulphur vapor, this being a triple point analogous to the point *O* in Fig. 78. The vapor pressure curves of rhombic and monoclinic sulphur are represented by *OB* and *OA* respectively. The dotted curve *OA'* which is a continuation of *OA* is the vapor-pressure curve of monoclinic sulphur in a metastable region. In like manner *OB'* represents the vapor-pressure curve of rhombic sulphur in the metastable condition, *B'* being a metastable melting point. As in the pressure-temperature diagram for water, the metastable phases have the higher vapor pressures. The effect of increasing pressure on the transition point O, is represented by the line OC. This is termed a *transition curve*, and, since increase in pressure raises the transition point, the line slopes away from the vertical axis. The effect of increased pressure on the melting-point of monoclinic sulphur is shown by the curve AC.

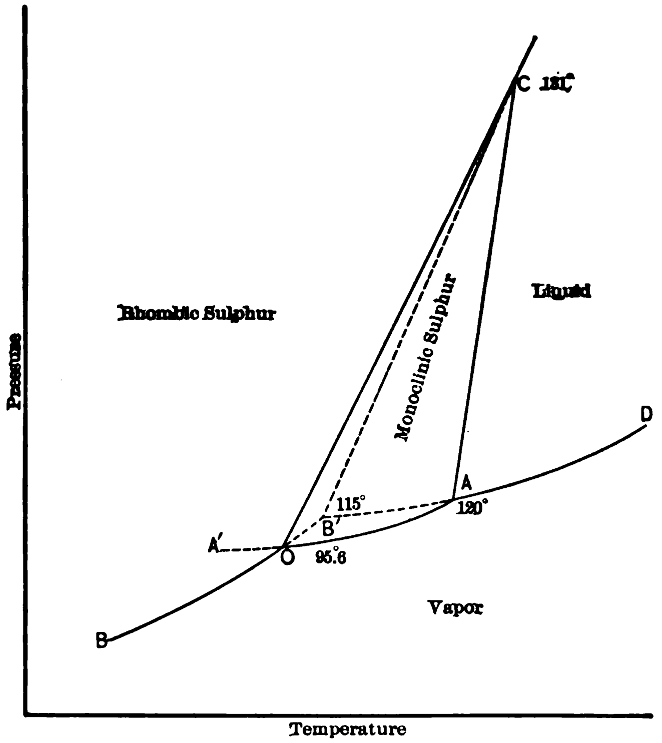


Fig. 79.

This also slopes away from the vertical axis, but the change in the melting-point of monoclinic sulphur produced by a given change in pressure being less than the corresponding change in the transition point, the two curves, OC and AC, intersect at the point C. The point C corresponds to a temperature of 131° C. and a pressure of 400 atmospheres. The vapor-pressure curve of stable liquid sulphur is represented by the curve AD. The vapor-pressure curve of the metastable liquid phase is represented by the curve AB' which is continuous with AD. The diagram is completed by the curve $B'C$ which represents the effect of pressure on the metastable melting-point of rhombic sulphur. Monoclinic sulphur does not exist above the point C; hence when liquid sulphur is allowed to solidify at pressures exceeding 400 atmospheres, the rhombic modification is formed, whereas under ordinary pressures the monoclinic modification appears first.

The phase rule enables us to state the exact conditions required for equilibrium in this system and to check the results of experiment. Thus, according to the formula, $C - P + 2 = F$, since $C = 1$, the system will be non-variant when $P = 3$. Since there are four phases involved, theoretically any three of these may be co-existent and four triple points are possible. The theoretically-possible triple points are as follows: —

(1) Rhombic sulphur, monoclinic sulphur, and vapor (O);
(2) Rhombic sulphur, monoclinic sulphur, and liquid (C);
(3) Rhombic sulphur, liquid, and vapor (B');
(4) Monoclinic sulphur, liquid and vapor (A).

In this particular system all of the four possible triple points can be realized experimentally. That this is the case is due to the comparative slowness of the change from rhombic to monoclinic sulphur above the triple point. If this change were rapid it is evident that all of the theoretically-possible non-variant systems could not be realized experimentally.

As in the case of water, the curves in the diagram represent univariant systems and the areas bivariant systems. The student is advised to tabulate the univariant and bivariant systems represented in the pressure-temperature diagram for sulphur.

Two-component Systems. Turning now to two-component systems we are confronted with a more difficult problem, and one which includes many special cases. Thus, we may have cases of anhydrous salts and water, hydrated salts and water, volatile solutes, two liquid phases, consolute liquids, and solid solutions. To enter upon a discussion of these would not be profitable, since they only serve to give greater emphasis to the general truth of the phase rule. We shall select a few typical two-component systems for consideration here.

(a) *Anhydrous Salt and Water.* In the equilibrium diagram of water (here represented by dotted lines, Fig. 80), we designate the triple point by O. At this point ice and water have the same vapor pressure. Similarly, a solution at its freezing-point has the same vapor pressure as the ice which separates. The intersection of the vapor-pressure curve for ice, OB, and the vapor-pressure curve of the solution of the anhydrous salt, $O''A''$, determines a new triple point O''. Since the presence of the dissolved salt tends to diminish the vapor pressure of water, the curve $O''A''$ is situated below the curve OA, and for the same reason the triple point O'' is found to the left of O. If now we keep an excess of dissolved substance continually present, all of the liquid phases

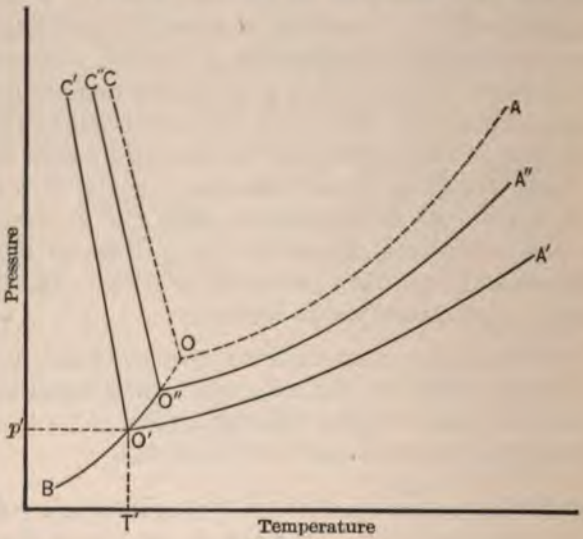


Fig. 80.

which are formed will of necessity be saturated solutions. When these solutions finally freeze they will furnish, not pure ice, but a mixture of ice and solid salt, known as a *cryohydrate*. By a partial freezing we can therefore obtain the system: Solid salt, ice, saturated solution and vapor, or in other words, a system of $n + 2$ phases of which the existence is only possible at the freezing temperature T' of the saturated solution, and under the pressure p' corresponding to the vapor pressure of ice and the saturated solution. These conditions are represented in the diagram by the quadruple point O'. If now we pass from the point O', increasing the temperature and pressure as prescribed by the curve $O'A'$, the ice disappears, while the salt, the saturated solution, and the vapor furnish a series of 3-phase systems. Again starting from the point O' and lowering the temperature and the pressure as indicated by the curve $O'B$, the liquid phase disappears, while the solid salt, ice, and vapor constitute another series of 3-phase systems. This, of course, is on the supposition that the vapor pressure of the solid salt is negligible. Finally, a considerable increase in pressure causes a slight lowering of the temperature corresponding to the quadruple point, the conditions being represented by the curve $O'C'$.

All possible non-saturated solutions of the salt will be represented by points within the area, $AOO'A'$. Thus, let $O''A''$ represent the vapor-pressure curve of a dilute solution of the salt in water. The freezing-point of this solution is represented by the point O'', while $O''C''$ represents the variation of the freezing-point of the solution with pressure.

The following table summarizes the possibilities indicated by the phase rule: —

4 phases; salt, ice, saturated solution, vapor (point, O');
3 phases; salt, saturated solution, vapor (curve, $O'A'$);
3 phases; salt, ice, vapor (curve, $O'B$);
3 phases; salt, ice, saturated solution (curve, $O'C'$);
2 phases; salt, saturated solution (area, $C'O'A'$);
2 phases; salt, water vapor (area, $BO'A'$);
2 phases; salt, ice (area, $BO'C'$);

3 phases; ice, non-saturated solution, vapor (curve, *OO′*);
2 phases; non-saturated solution, vapor }
1 phase; non-saturated solution } (area, *AOO′A′*);
2 phases; non-saturated solution, ice }
1 phase; non-saturated solution } (area, *COO′C′*).

As will be seen, there is only one non-variant point in the entire diagram, viz., the point *O′*. In this system there are three degrees of freedom, since in addition to temperature and pressure the concentration of the solution may also be varied.

The pressure-temperature diagram (Fig. 80) having been discussed, we now turn to the concentration-temperature diagram for the same system, Fig. 81. In this diagram the abscissæ represent temperatures and the ordinates, concentrations. For convenience, corresponding points in Figs. 80 and 81 will be designated by the same letters. The equilibrium between ice, water and water vapor is represented by the point *O*. If now a small

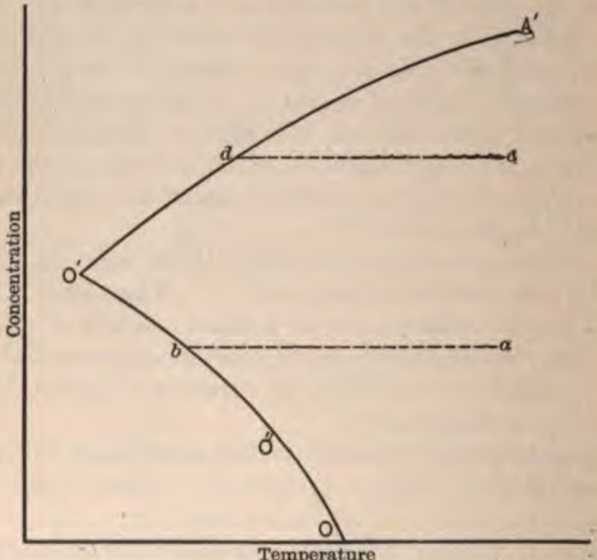


Fig. 81.

amount of anhydrous salt be added to the water, the freezing-point will be lowered to O''. As the proportion of salt is increased the temperature of equilibrium is lowered along the curve $OO''O'$. A point is ultimately reached at which the solution becomes saturated, and on further addition of salt it is not dissolved, but remains in contact with the ice and saturated solution. This is the cryohydric point, and represents the lowest temperature which can be obtained in this particular system. The diagram is completed by the solubility curve of the salt, $O'A'$. Each point on this curve represents the concentration of the saturated solution at all temperatures, from the critical temperature of the solution to the cryohydric temperature. The meaning of the concentration-temperature diagram may be made clearer by a consideration of the behavior of a solution when gradually cooled. Let *a* represent a dilute solution of the anhydrous salt. On lowering the temperature along *ab*, no change will occur until the curve OO' is reached; then ice will begin to separate and as the cooling is continued, the composition of the solution will change along OO' until it reaches the cryohydric point O'. Here both salt and ice will separate, and the solution will solidify completely at the temperature corresponding to the point O'. In like manner, if we start with a concentrated solution represented by the point *c* and cool along *cd* no change will take place until the curve $O'A'$ is reached; then solid salt will separate and the composition of the solution will alter along $O'A'$ until the temperature is reduced to that corresponding to the cryohydric point, when the whole solution will solidify as in the previous case. This phenomenon was first systematically investigated by Guthrie * who concluded that such mixtures of constant composition and definite melting-point are chemical compounds, and, therefore, he proposed to call them cryohydrates. It has since been shown that cryohydrates are not definite chemical compounds. Among the various reasons which have been advanced to prove the incorrectness of Guthrie's views, the following are the most cogent: — (1) the physical properties of a cryohydrate are the mean of the corresponding properties of the constituents, this being rarely true of chemical compounds; (2) the lack of homogeneity of a cryohydrate can be detected under the microscope; and (3) the constituents are seldom present in simple molecular proportions.

---

* Phil. Mag. [4], **49**, 1 (1875); [5], **1**, 49 and **2**, 211 (1876).

Applying the phase rule to the above two-component system, it is evident that there is but one non-variant system: this is represented by the point *O′*. When three phases are co-existent the system is univariant, when only two phases are present the system is bivariant, and finally, when only one phase is present the system acquires three degrees of freedom or is trivariant. It is evident that a system having three degrees of freedom cannot be completely represented by a diagram in a single plane. It is possible, however, to construct a three-dimensional model which will represent the equilibrium very satisfactorily. Such a model is shown in Fig. 82, the lettering being made to correspond with that of the two diagrams, Figs. 81 and 82, from which it is derived.

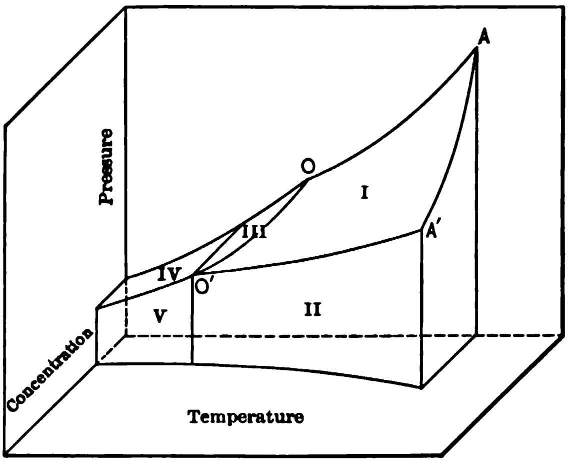


Fig. 82.

I. Unsaturated Solution.
II. Salt and Saturated Solution.
III. Ice and Unsaturated Solution.
IV. Ice and Cryohydrate.
V. Salt and Cryohydrate.

(b) *Hydrated Salt and Water.* An interesting example is furnished by the system — ferric chloride and water. This system has been very carefully investigated by Roozeboom.* The concentration-temperature diagram, plotted from Roozeboom's data, is given in Fig. 83. The freezing-point of pure water is represented by *A*, and the lowering of the freezing-point produced by the addition of ferric chloride is indicated by the curve *AB*. At the cryohydric temperature, – 55° C., ice, $Fe_2Cl_6 \cdot 12\,H_2O$, saturated solution, and vapor are in equilibrium, and the system is non-variant. On adding more ferric chloride, the ice phase disappears, and the univariant system, $Fe_2Cl_6 \cdot 12\,H_2O$, saturated solution, and vapor results. The equilibrium is represented by the curve *BC* which may be regarded as the solubility curve of the dodecahydrate. On continuing the addition of ferric chloride, the temperature continues to rise until the point *C* is reached. Here the composition of the solution is identical with that of the dodecahydrate, and, therefore, the temperature corresponding to this point, 37° C., may be looked upon as the melting-point of $Fe_2Cl_6 \cdot 12\,H_2O$. Further addition of ferric chloride will naturally

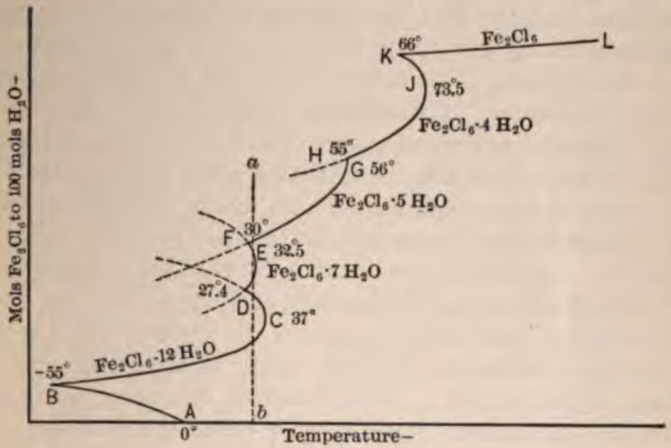


Fig. 83.

---

* Zeit. phys. Chem., **4**, 31 (1889); **10**, 477 (1892).

lower the melting point and the equilibrium will alter along the curve *CD*. It is thus possible to have two saturated solutions, one of which contains more water and the other less, than the hydrate which is in equilibrium with the solution. These solutions are both stable throughout and are nowhere supersaturated. Roozeboom was the first investigator to discover a saturated solution containing less water than the solid hydrate with which it is in equilibrium. This discovery led him to define supersaturation as follows: — "A solution is supersaturated with respect to a solid phase at a given temperature if its composition is between that of the solid phase and the saturated solution." At the point *D* the curve reaches another minimum which is analogous to the point *B*, except that the heptahydrate, $Fe_2Cl_6 \cdot 7\ H_2O$, takes the place of ice. Here we have equilibrium between the dodecahydrate, the heptahydrate, saturated solution, and vapor, and the system is non-variant. On further addition of ferric chloride another maximum is reached at *E*, corresponding to the melting-point of the heptahydrate. In a similar manner, two other maxima at greater concentrations of ferric chloride reveal the existence of the hydrates, $Fe_2Cl_6 \cdot 5\ H_2O$, and $Fe_2Cl_6 \cdot 4\ H_2O$.

At the three remaining quadruple points the following phases are in equilibrium:—At *F*, $Fe_2Cl_6 \cdot 7\ H_2O$, $Fe_2Cl_6 \cdot 5\ H_2O$, saturated solution and vapor; at *H*, $Fe_2Cl_6 \cdot 5\ H_2O$, $Fe_2Cl_6 \cdot 4\ H_2O$, saturated solution and vapor; and at *K*, $Fe_2Cl_6 \cdot 4\ H_2O$, Fe_2Cl_6, saturated solution and vapor. The solubility of the anhydrous salt is represented by the curve *KL*. Metastable solubility and melting-point curves are represented by dotted lines.

The student should apply the phase rule to this system. If a fairly dilute solution of ferric chloride is evaporated at 31° C., the water gradually disappears and a residue of the dodecahydrate remains. This residue then liquefies and again dries down, the composition of the residue corresponding to the heptahydrate: on further standing the phenomenon is repeated, the final and permanent residue having a composition corresponding to the pentahydrate. The dotted line *ab* shows the isothermal along which the composition varies. It would have been a difficult matter to explain the alternations of moisture and dryness observed in this experiment without the concentration-temperature diagram.

Alloys. Among the most interesting two-component systems known are those involving mixtures of metals, or *alloys*. These have been made the subject of systematic investigations by numerous experimenters among whom may be mentioned Roberts-Austen, Charpy, Roozeboom, and Heycock and Neville. We have space to consider only two comparatively-simple cases.

(a) *Alloys of Silver and Copper.* The conditions of equilibrium in this binary system have been studied by Heycock and Neville.* The two components, silver and copper, are not miscible in the solid state and do not combine chemically. To determine the curves of equilibrium, mixtures of the two metals in varying proportions were fused and then allowed to cool slowly, the rate of cooling being observed with a thermocouple, one junction of which was maintained at constant temperature, while the other junction was placed in the mixture of molten metals. The terminals of the thermocouple were connected to a sensitive galvanometer graduated to read directly in degrees, and the rate of cooling was followed by the movement of the needle of the galvanometer. As the mixture cooled, two "breaks" were observed; the first of these varied with the composition of the mixture, while the second remained practically constant at 777° C. When the temperatures corresponding to the first break are plotted as ordinates against the composition of the mixture as abscissæ, the diagram shown in Fig. 84 is obtained.

The point A represents the freezing-point of pure silver, B that of pure copper, the curve AO represents the effect of the gradual addition of copper upon the freezing-point of silver, and BO the effect of silver on the freezing-point of copper. The intersection of the two curves at O corresponds to an alloy containing 40 atomic per cent of copper. This lowest melting mixture is known as the *eutectic* (εὖ = well, and τήκειν = melt) mixture. At O the system is non-variant, silver, copper, solution and vapor being in equilibrium. The solid which separates at O, having a more uniform texture than that of all other mixtures of the two components, is known as the eutectic alloy. When the composition of a mixture of two metals corresponds to that of the eutectic alloy, the two metals crystallize simultaneously in minute separate crystals. When examined under the microscope the solid eutectic alloy will be seen to be a conglomerate of very small crystals, whereas all of the other alloys of the same metals will be found to contain large crystals of either one or the other component embedded in the conglomerate. While the composition of the eutectic alloy in the above system is found to correspond very closely to the formula Ag_3Cu_2, yet the nature of the equilibrium curves proves it to be nothing more than a mechanical mixture of the two metals. The meaning of the diagram will be clearer from a careful consideration of the phenomena accompanying the cooling of a mixture of the molten metals.

---

* Phil. Trans., 189, 25 (1897).

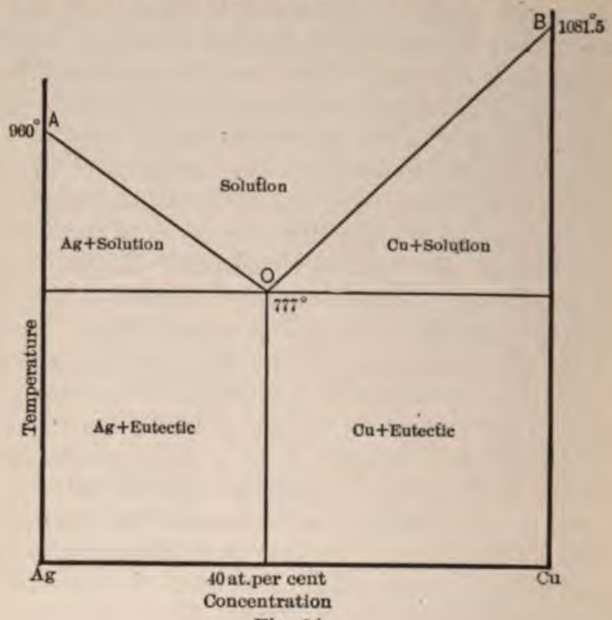


Fig. 84.

Take for example, a fused mixture relatively rich in silver. As the temperature falls, a point will ultimately be reached at which pure silver begins to separate, and since the temperature remain constant during the solidification, a break occurs in the coolin curve. This first break corresponds to a point on the curve *AO* As silver continues to separate, the composition of the mixture changes along *AO*, until when *O* is reached, the mixture is saturated with respect to copper, and both metals separate as a conglomerate having the same composition as the fused mixture The separation of the eutectic alloy causes the second break i the cooling curve, the temperature remaining constant until the entire mass has solidified. It will be noticed that this system is th exact analogue of the system—anhydrous salt and water; the eutectic point and the cryohydric point representing identical conditions

(b) *Alloys of Gold and Aluminium.* This system has bee studied by Roberts-Austen.* The equilibrium curves in th concentration temperature diagram, Fig. 85, reveal the existenc

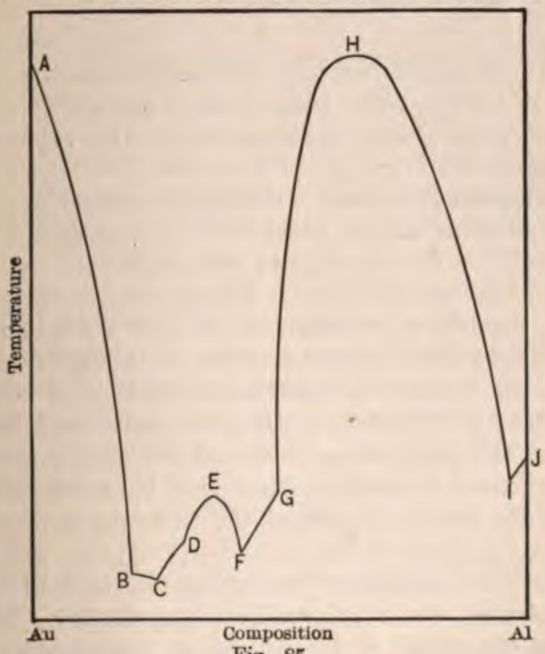


Fig. 85.

---

* Phil. Trans. A., 194, 201 (1900).

of definite compounds, Au_5Al_2, Au_2Al, and $AuAl_2$, corresponding to the points *D*, *E*, and *H* respectively. The discontinuities at *B* and *G* suggest the possibility of two other compounds, *viz.*, Au_4Al and AuAl. The diagram shows that the following substances will crystallize in succession from the molten alloy, these being the different solids with which the liquid mixture is saturated in its successive stages of equilibrium: —

Curve *AB*, pure gold at *A*;
Curve *BC*, Au_4Al, nearly pure at *B*;
Curve *CD*, Au_5Al_2 or Au_8Al_3, nearly pure at *D*;
Curve *DEF*, Au_2Al, pure at *E*;
Curve *FG*, AuAl, maximum undetermined;
Curve GHI, $AuAl_2$, pure at *H*;
Curve *IJ*, Al, pure at *J*.

The points *C*, *F*, and *I* represent non-variant systems, the melting points of the respective eutectic alloys being 527°, 569°, and 647°. This system in many respects resembles the system — ferric chloride and water.

Three-component Systems. When three components are present, the equilibria become much more complicated. Applying the formula, $C - P + 2 = F$, we find that it is necessary to have five phases co-existent for a non-variant system, four for a univariant, three for a bivariant, and two for a trivariant. The most satisfactory method of representing equilibria in three-component systems is that in which use is made of the triangular diagram. The three corners of an equilateral triangle are taken to represent the pure components, and the composition of any mixture, expressed in atomic percentages, is represented by the position of the center of mass of the three components within the triangle.

For example, in the system, — potassium nitrate, sodium nitrate, and lead nitrate, carefully investigated by Guthrie,* the three components are placed at the corners of the triangle shown in

---

* Phil. Mag., 5, **17**, 472 (1884).

Fig. 86. The melting-point of pure potassium nitrate is 340° and that of pure sodium nitrate is 305°. The melting-point of pure lead nitrate cannot be determined since the salt decomposes before its melting-point is reached. The eutectic mixtures of the three pairs of salts are represented by the points *D*, *E*, and *F* respectively. In like manner *O* represents the melting point of the non-variant system, — potassium nitrate, sodium nitrate, lead nitrate, fused mixture of the three salts, and vapor. In order to represent temperature, use is frequently made of a triangular prism in which the altitude is taken as the temperature axis, the resulting surface within the prism representing the variation of the equilibrium with temperature.*

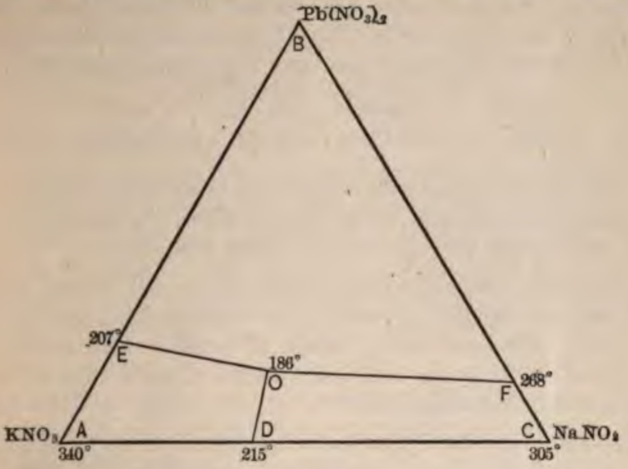


Fig. 86.

PROBLEMS.

1. The vapor pressure of solid NH_4HS at 25°.1 is 50.1 cm. Assuming that the vapor is practically completely dissociated into NH_3 and H_2S, calculate the total pressure at equilibrium when solid NH_4HS is allowed

---

* For a complete treatment of three-component systems as well as for a clear presentation of the phase rule, the student should consult "The Phase Rule and Its Applications," by Alexander Findlay.

to dissociate at 25°.1 in a vessel containing ammonia at a pressure of 32 cm. *Ans.* 59.5 cm.

2. In the partition of acetic acid between CCl_4 and water, the concentration of the acetic acid in the CCl_4 layer was c gram-molecules per liter and in the corresponding water layer w gram-molecules per liter.

c	0.292	0.363	0.725	1.07	1.41
w	4.87	5.42	7.98	9.69	1.07

Acetic acid has its normal molecular weight in aqueous solutions. From these figures show that, at these concentrations, the acetic acid in the carbon tetrachloride solution exists as double molecules.

3. Acetic acid distributes itself between water and benzene in such a manner that in a definite volume of water there are 0.245 and 0.314 gram of the acid, while in an equal volume of benzene there are 0.043 and 0.071 gram. What is the molecular weight of acetic acid in benzene, assuming it to be normal in water? *Ans.* 121.3.

4. The salt $Na_2HPO_4.12\ H_2O$ has a vapor pressure at 15° of 8.84 mm., and at 17°.3 of 10.53 mm. Calculate the heat of vaporization, *i.e.*, the thermal change during the loss of 1 mol of water of crystallization by evaporation. *Ans.* $-12{,}651$ cal.

5. The solubility of boric acid in water is 38.45 grams per liter at 13°, and 49.09 grams per liter at 20°. Calculate the heat of solution of boric acid per mol. *Ans.* $-5{,}822$ cal.

6. Plot the pressure-temperature diagram for calcium carbonate from the table given on p. 280, and apply the phase rule.

7. Is it possible to decide by the phase rule whether the eutectic alloy is a mixture or a compound?

CHAPTER XVII.

CHEMICAL KINETICS.

Velocity of Reaction. In the two preceding chapters we have considered the equilibrium which is established when the speeds of the direct and reverse reactions have become equal. We now proceed to consider the velocity of individual reactions. By far the greater number of the reactions between inorganic substances proceed with such rapidity that it is impossible to measure their velocities. Thus, when an acid is neutralized by a base, the indicator changes color almost instantly. There are a few well-known reactions which are exceptions to this rule; among these may be mentioned the oxidation of sulphur dioxide and the decomposition of hydrogen peroxide. Both of these reactions are well adapted to kinetic experiments. In organic chemistry, on the other hand, slow reactions are the rule rather than the exception. Thus the reaction between an alcohol and an acid forming an ester and water, proceeds very slowly under ordinary conditions and the progress of the reaction may be easily followed: By means of the law of mass action it is possible to derive equations expressing the velocity of a reaction at any moment in terms of the concentrations of the reacting substances present at that time.

Let the equation

$$A_1 + A_2 \rightleftarrows A_1' + A_2'$$

represent a reversible reaction and let a, b, c, and d be the respective initial concentrations of the reacting substances A_1, A_2, A_1', and A_2'. The velocity of the direct reaction will then be

$$\frac{dx}{dt} = k\ (a - x)\ (b - x), \tag{1}$$

where k is the velocity constant, and dx is the infinitely small increase in the amount of x during the infinitely small interval of time dt. Similarly the velocity of the reverse reaction will be

$$\frac{dx'}{dt} = k_1\ (c + x)\ (d + x). \tag{2}$$

It is evident that the substances on the right-hand side of the equation will exert an ever-increasing influence upon the velocity of the direct reaction, which must accordingly decrease. When, however, the velocities of the direct and reverse reactions become equal, equilibrium will be established, and the ratio of the amounts of the reacting substances on the two sides of the equation will remain constant. The total velocity due to these opposing reactions will be

$$\frac{dX}{dt} = \frac{dx}{dt} - \frac{dx'}{dt} = k\,(a - x)\,(b - x) - k_1\,(c + x)\,(d + x) \tag{3}$$

and at equilibrium, when $\frac{dX}{dt} = 0$,

$$k\,(a - x)\,(b - x) = k_1\,(c + x)\,(d + x),$$

or

$$\frac{(c + x)\,(d + x)}{(a - x)\,(b - x)} = \frac{k}{k_1} = K_c. \tag{4}$$

This equation has been thoroughly tested in the two preceding chapters. Thus, in the reaction

$$C_2H_5OH + CH_3COOH \rightleftarrows CH_3COOC_2H_5 + H_2O,$$

K_c has been shown to have the value, 2.84, at ordinary temperatures. The velocity constants of the direct and reverse reactions have also been determined, the values being, $k = 0.000238$ and $k_1 = 0.000815$. When these values are substituted in the equation, $\frac{k}{k_1} = K_c$, we obtain $K_c = 2.92$, a value which agrees well with that found by direct experiment. The application of equation (3) is much simplified by the fact that most reactions proceed nearly to completion in one direction, so that the term $k_1\ (c + x)$ $(d + x)$ will be so small that it may be neglected. We then have

$$\frac{dx}{dt} = k\,(a - x)\,(b - x), \tag{5}$$

an equation expressing the velocity of the direct reaction in terms of the concentrations of the reacting substances.

Unimolecular Reactions. The simplest type of chemical reaction is that in which only one substance undergoes change and in which the velocity of the reverse reaction is negligible. The decomposition of hydrogen peroxide is an example of such a reaction. In the presence of a catalyst, such as certain unorganized ferments or collodial platinum, hydrogen peroxide decomposes as represented by the equation,

$$2\,H_2O_2 \rightleftarrows 2\,H_2O + O_2.$$

This reaction is usually allowed to take place in dilute aqueous solution so that there is no appreciable alteration in the amount of solvent throughout the entire course of the reaction. Furthermore, the activity of the catalyst remains constant so that the course of the reaction is wholly determined by the concentration of the hydrogen peroxide. A very satisfactory catalyst is hæmase, an enzyme derived from blood. The concentration of hydrogen peroxide present at any time during the reaction can be determined very simply by removing a definite portion of the reaction mixture, adding an excess of sulphuric acid to destroy the activity of the hæmase, and then titrating with a standard solution of potassium permanganate.

The following table gives the results of such an experiment: —

t (minutes).	$a-x$, cc. $KMnO_4$.	x, cc. $KMnO_4$.	k
0	46.1	0	......
5	37.1	9.0	0.0435
10	29.8	16.3	0.0438
20	19.6	26.5	0.0429
30	12.3	33.8	0.0440
50	5.0	41.1	0.0444
			Mean 0.0437

The second column of the table gives the number of cubic centimeters of the potassium permanganate solution required to oxidize 25 cc. of the reaction mixture when the time intervals recorded in the first column have elapsed after the introduction of the catalyst. Since the numbers in the second column represent the actual concentration of hydrogen peroxide present at the end of the successive intervals of time, it is evident that the difference between these numbers and 46.1 cc. — the initial concentration of hydrogen peroxide — will give the amounts of peroxide decomposed in those intervals. These numbers are recorded in the third column of the table. It will be seen that as the concentration of the hydrogen peroxide decreases the rate of the reaction diminishes. Thus, in the first interval of 10 minutes, an amount of hydrogen peroxide corresponding to $46.1 - 29.8 = 16.3$ cc. of potassium permanganate is decomposed, while in the second interval of 10 minutes, the amount of hydrogen peroxide decomposed is equivalent to $29.8 - 19.6 = 10.2$ cc. of potassium permanganate. Since only a single substance is undergoing change, equation (5) simplifies to the following form: —

$$\frac{dx}{dt} = k\,(a - x).$$

It is impossible to apply the equation in this form, since in order to obtain accurate titrations, dt must be taken fairly large and during this interval of time $a - x$ would have diminished. Approximate values of k may be obtained by taking the average value of $a - x$ during the interval dt within which an amount dx of hydrogen peroxide is being decomposed. For example, let us take the interval between 5 and 10 minutes; $dx = 16.3 - 9.0 = 7.3$ cc., $dt = 5$ min., and the average value of $a - x$ is

$$\frac{37.1 + 29.8}{2} = 33.45 \text{ cc.}$$

Substituting in the equation

$$\frac{dx}{dt} = k\,(a - x),$$

we have

$$\frac{7.3}{5} = k \times 33.45,$$

and

$$k = 0.0436.$$

Similarly taking the next interval between 10 and 20 minutes; $dx = 26.5 - 16.3 = 10.2$ cc., $dt = 10$ minutes, and the average value of $a - x$ is $\frac{29.8 + 19.6}{2} = 24.7$ cc. Substituting in the equation as before, we obtain

$$\frac{10.2}{10} = k \times 24.7,$$

and

$$k = 0.0413.$$

As will be seen these two values of k are not in good agreement, although the first value of k agrees closely with the mean value of k given in the fourth column of the table.

In order to apply the equation

$$\frac{dx}{dt} = k\,(a - x)$$

it must be integrated.*

The integration of this equation may be performed as follows: —

$$\frac{dx}{dt} = k\,(a - x),$$

therefore

$$\frac{dx}{a - x} = k\,dt\cdot$$

Integrating, we have

$$\int \frac{dx}{a - x} - \int k\,dt = \text{constant} = C,$$

therefore

$$-\log_e(a - x) - kt = C.$$

In order to determine C, the constant of integration, we make use of the experimental fact that when $t = 0$, $x = 0$. Substituting these values, we have

$$-\log_e a = C.$$

Consequently

$$\log_e a - \log_e(a - x) = kt,$$

or

$$\frac{1}{t}\log_e \frac{a}{a - x} = k.$$

---

* The student who is unfamiliar with the Calculus must take the result of this calculation for granted.

Passing to Briggsian logarithms, we obtain

$$\frac{1}{t}\log\frac{a}{a-x} = 0.4343\,k.$$

By substituting in this equation the corresponding values of a, $a-x$, and t from the preceding table, the values of k given in the fourth column of the table are obtained.

The equation

$$\frac{dx}{dt} = k\,(a-x),$$

may also be thrown into an exponential form, as follows: —

Since

$$\frac{1}{t}\log_e\frac{a}{a-x} = k,$$

we may write,

$$-\,kt = \log_e\frac{a-x}{a},$$

or

$$a - x = ae^{-kt},$$

and

$$x = a\,(1 - e^{-kt}).$$

In this equation k may be regarded as the fraction of the total amount of substance decomposing in the unit of time, provided this unit is so small that the quantity at the end of the time unit is only slightly different from that at the beginning. The time required for one-half of the substance to change, is known as the period of half-change, T, and may be calculated from k by means of the equation

$$\log 2 = 0.4343\,kT,$$

therefore

$$T = 0.6943\,\frac{1}{k},$$

or

$$\frac{1}{k} = 1.443\,T.$$

Reactions in which only one mol of a single substance undergoes change are known as *unimolecular reactions*, or *reactions of the* *first order.* In a unimolecular reaction, the velocity constant k, is independent of the units in which concentration is expressed. If, in the integrated equation

$$kt = \log_e \frac{a}{a - x},$$

t becomes infinite, then $x = a$. In other words, for finite values of t, x must always remain less than a and the reaction will never proceed to completion.

Another unimolecular reaction which has been thoroughly investigated, is the hydrolysis of cane sugar. When cane sugar is dissolved in water containing a small amount of free acid it is slowly transformed into d-glucose and d-fructose. The velocity of the reaction is very small and is dependent upon the strength of the acid added. The progress of the reaction may be very easily followed by means of the polarimeter. Cane sugar itself is dextro-rotatory, while d-fructose rotates the plane of polarization more strongly to the left than d-glucose rotates it to the right. Therefore, as the hydrolysis proceeds, the angle of rotation to the right steadily diminishes until, when the reaction is complete, the plane of polarization will be found to be rotated to the left. On this account the hydrolysis of cane sugar is commonly termed *inversion* and the molecular mixture of d-fructose and d-glucose constituting the product of the reaction is called *invert sugar.* Let α_0 denote the initial angle of rotation, at the time $t = 0$, due to a mols of cane sugar, let α_0' denote the angle of rotation when inversion is complete and let α be the angle of rotation at any time t; then since rotation of the plane of polarization is proportional to the concentration x, the amount of cane sugar inverted, will be

$$x = a\frac{\alpha_0 - \alpha}{\alpha_0 + \alpha_0'}.$$

In the equation

$$C_{12}H_{22}O_{11} + H_2O \rightleftarrows C_6H_{12}O_6 + C_6H_{12}O_6,$$

representing the inversion of cane sugar, the velocity of the reaction will be, according to the law of mass action, proportional to the molecular concentrations of the cane sugar and the water.

Since the reaction takes place in the presence of such a large excess of water, its effect may be considered to be constant. The velocity of the reaction is then proportional to the active mass of the sugar alone, or in other words the reaction is unimolecular. In the differential equation expressing the velocity of a unimolecular reaction,

$$\frac{dx}{dt} = k\,(a - x),$$

we have

$$k = \frac{1}{t} \log_e \frac{a}{a - x};$$

and since a and x are measured in terms of angles of rotation of the plane of polarization, we have

$$k = \frac{1}{t} \log_e \frac{\alpha_0 + \alpha_0'}{\alpha + \alpha_0'}.$$

The following table gives the results obtained with a 20 per cent solution of cane sugar in the presence of 0.5 molar solution of lactic acid at 25° C.

t (minutes).	α	k
0	34°.5	....
1,435	31°.1	0.2348
4,315	25°.0	0.2359
7,070	20°.16	0.2343
11,360	13°.98	0.2310
14,170	10°.01	0.2301
16,935	7°.57	0.2316
19,815	5°.08	0.2991
29,925	− 1°.65	0.2330
Inf.	−10°.77	....

Bimolecular Reactions. When two substances react and the concentration of each changes, the reaction is *bimolecular or of the second order*. Let a and b represent the initial molar concentrations of the two reacting substances and let x denote the amount transformed in the interval of time t; then the velocity of the reaction will be expressed by the equation

$$\frac{dx}{dt} = k\,(a - x)\,(b - x).$$

The simplest case is that in which the two substances are present in equivalent amounts. Under these conditions the velocity equation becomes

$$\frac{dx}{dt} = k\,(a - x)^2.$$

This equation may be integrated as follows: —*

$$k\,dt = \frac{dx}{(a - x)^2},$$

$$k\int_{t_1}^{t_2} dt = \int_{x_1}^{x_2} \frac{dx}{(a - x)^2},$$

therefore

$$k\,(t_2 - t_1) = \left[\frac{1}{a - x}\right]_{x_1}^{x_2} = \frac{x_2 - x_1}{(a - x_1)\,(a - x_2)},$$

or

$$k = \frac{1}{(t_2 - t_1)} \cdot \frac{(x_2 - x_1)}{(a - x_1)\,(a - x_2)}.$$

If time be reckoned from the beginning of the reaction, then $x_1 = 0$ and $t = 0$, and we have

$$k = \frac{1}{t} \cdot \frac{x}{a\,(a - x)}.$$

If the reacting substances are not present in equivalent amounts then the velocity equation becomes

$$\frac{dx}{dt} = k\,(a - x)\,(b - x).$$

Assuming that time is measured from the beginning of the reaction, the integration of this equation may be performed as follows: —

$$k\int_0^t dt = \int_0^x \frac{dx}{(a - x)\,(b - x)}.$$

Decomposing into partial fractions,

$$kt = \frac{1}{a - b}\left[\int_0^x \frac{dx}{b - x} - \int_0^x \frac{dx}{a - x}\right],$$

---

* The student who is unfamiliar with the Calculus must take the results of these calculations for granted.

therefore

$$kt = \frac{1}{a-b}\Big[\log_e \frac{a-x}{b-x}\Big]_0^x,$$

or

$$kt = \frac{1}{a-b}\log_e \frac{b\,(a-x)}{a\,(b-x)}.$$

Or passing to Briggsian logarithms,

$$0.4343\,k = \frac{1}{t\,(a-b)}\log \frac{b\,(a-x)}{a\,(b-x)}.$$

The value of k in a bimolecular reaction is not independent of the units in which the concentration is expressed, as is the case with a unimolecular reaction. Suppose that a unit 1/nth of that originally selected is used to express concentration, then the value of k in the equation

$$k = \frac{1}{t}\frac{x}{a(a-x)},$$

becomes

$$k' = \frac{1}{t}\cdot\frac{nx}{na\cdot n\,(a-x)} = \frac{1}{t}\cdot\frac{x}{na\,(a-x)}.$$

Thus, the value of k varies inversely as the numbers expressing the concentrations.

As an illustration of a bimolecular reaction we may take the hydrolysis of an ester by an alkali. The reaction

$$CH_3COOC_2H_5 + NaOH \rightleftarrows CH_3COONa + C_2H_5OH,$$

has been studied by Warder,* Reicher,† Arrhenius,‡ Ostwald§ and others. Arrhenius employed in his experiments 0.02 molar solutions of ester and alkali. These solutions were placed in separate flasks and warmed to 25° C. in a thermostat maintained at that temperature; equal volumes were then mixed, and at frequent intervals a portion of the reaction mixture was removed and titrated rapidly with standard acid. The accompanying table contains some of the results obtained: —

---

* Berichte, 14, 1361 (1881).

† Lieb. Ann., 228, 257 (1885).

‡ Zeit. phys. Chem., 1, 110 (1887).

§ Jour. prakt. Chem., 35, 112 (1887).

t (minutes).	$a-x$	k
0	8.04	......
4	5.30	0.0160
6	4.58	0.0156
8	3.91	0.0164
10	3.51	0.0160
12	3.12	0.0162
		Mean 0.0160

The numbers in the second column of the table represent the concentrations of sodium hydroxide and of ethyl acetate, expressed in terms of the number of cubic centimeters of standard acid required to neutralize 10 cc. of the reaction mixture. Owing to the high velocity of the reaction it is difficult to avoid large experimental errors, nevertheless the values of k given in the third column of the table will be observed to differ very slightly from the mean value.

Reicher investigated the same reaction when the reacting substances were not present in equivalent proportions. In this case, the progress of the reaction was followed by titrating definite portions of the reaction mixture from time to time, the excess of sodium hydroxide being determined by titrating a portion of the mixture at the expiration of twenty-four hours, when the ester was completely hydrolyzed. His results are given in the following table: —

t (minutes).	$a-x$ (alkali).	$b-x$ (ester).	k
0	61.95	47.03	....
4.89	50.59	35.67	0.00093
11.36	42.40	27.48	0.00094
29.18	29.35	14.43	0.00092
Inf.	14.92	0	....

Reicher also studied the effect of different bases upon the velocity of the reaction. He found for strong bases approximately equal values of k, but for weak bases the values were irregular and smaller than those obtained with the more completely ionized bases. Arrhenius pointed out that the hydrolyzing power of a base is proportional to the number of hydroxyl ions which it yields. Writing the equation for the above hydrolysis in terms of ions, we have

$$CH_3COOC_2H_5 + Na^{\cdot} + OH' \rightleftarrows CH_3COO' + Na^{\cdot} + C_2H_5OH.$$

It is evident from this equation that all bases furnishing the same number of hydroxyl ions should give identical values of k. We may, therefore, modify the fundamental differential equation as follows: —

$$\frac{dx}{dt} = k'\alpha\,(a - x)\,(b - x),$$

where α is the degree of ionization of the base.

Trimolecular Reactions. When equivalent quantities of three substances react, the reaction is *trimolecular or of the third order.* If the initial molar concentrations of the reacting substances are denoted by a, b, and c, and if x denotes the proportion of each which is transformed in the interval of time t, the velocity of the reaction will be represented by the differential equation

$$\frac{dx}{dt} = k\,(a - x)\,(b - x)\,(c - x).$$

If the substances are present in equivalent amounts, the equation becomes

$$\frac{dx}{dt} = k\,(a - x)^3,$$

an expression which is much less difficult to integrate.

The integration of this equation may be performed as follows.*

$$k\int_0^t dt = \int_0^x \frac{dx}{(a-x)^3},$$

---

* The student who is unfamiliar with the Calculus must take the results of these calculations for granted.

therefore

$$kt = \frac{1}{2}\left[\frac{1}{(a-x)^2}\right]_0^x,$$

$$= \frac{1}{2}\left[\frac{1}{(a-x)^2} - \frac{1}{a^2}\right],$$

hence

$$k = \frac{1}{t} \cdot \frac{x\,(2\,a - x)}{2\,a^2\,(a - x)^2}.$$

When the reacting substances are not taken in equivalent amounts, the integration of the velocity equation may be performed as follows: —

$$\frac{dx}{dt} = k\,(a - x)\,(b - x)\,(c - x),$$

therefore

$$k\,dt = \frac{dx}{(a - x)\,(b - x)\,(c - x)}.$$

Decomposing into partial fractions,

$$\frac{1}{(a - x)\,(b - x)\,(c - x)} = \frac{A}{a - x} + \frac{B}{b - x} + \frac{C}{c - x}.$$

Multiplying through by $(a - x)$, we obtain

$$\frac{1}{(b - x)\,(c - x)} = A + (a - x)\left\{\frac{B}{b - x} + \frac{C}{c - x}\right\}.$$

Let $x = a$, then

$$A = - \frac{1}{(a - b)\,(c - a)}.$$

Similarly, multiplying by $(b - x)$ and $(c - x)$, and then placing $x = b$, and $x = c$, we have

$$B = - \frac{1}{(a - b)\,(b - c)},$$

and

$$C = - \frac{1}{(b - c)\,(c - a)}.$$

Then we obtain by substitution

$$\int_0^x \frac{dx}{(a - x)\,(b - x)\,(c - x)} = - \frac{1}{(a - b)\,(c - a)} \int_0^x \frac{dx}{a - x}$$

$$- \frac{1}{(a - b)\,(b - c)} \int_0^x \frac{dx}{b - x} - \frac{1}{(b - c)\,(c - a)} \int_0^x \frac{dx}{c - x}$$

Therefore,

$$kt = \left[-\frac{1}{(a-b)(c-a)}\log_e a\right]_0^x - \left[\frac{1}{(a-b)(b-c)}\log_e b\right]_0^x - \left[\frac{1}{(b-c)(c-a)}\log_e c\right]_0^x,$$

or

$$k = \frac{1}{t}\cdot\frac{\log_e\left(\frac{a-x}{a}\right)^{(b-c)}\cdot\log_e\left(\frac{b-x}{b}\right)^{(c-a)}\cdot\log_e\left(\frac{c-x}{c}\right)^{(a-b)}}{(a-b)(b-c)(c-a)}.$$

In a trimolecular reaction, k is inversely proportional to the square of the original concentration.

A typical trimolecular reaction is that between ferric and stannous chlorides. This reaction, represented by the following equation

$$2\,FeCl_3 + SnCl_2 \rightleftarrows 2\,FeCl_2 + SnCl_4,$$

has been investigated by A. A. Noyes.* Dilute solutions of the reacting substances were mixed at constant temperature, and definite portions of the reaction mixture were removed at measured intervals of time and titrated for ferrous iron. Before titrating with a standard solution of potassium permanganate it was necessary to decompose the stannous chloride present with mercuric chloride. The following table gives the results obtained with 0.025 molar solutions of ferric chloride and stannous chloride.

t (minutes).	$a-x$	x	k
2.5	0.02149	0.00351	113
3	0.02112	0.00388	107
6	0.01837	0.00663	114
11	0.01554	0.00946	116
15	0.01394	0.01106	118
18	0.01313	0.01187	117
30	0.01060	0.01440	122
60	0.00784	0.01716	122
			Mean 116

Noyes also found that the velocity of the reaction is accelerated more by an excess of ferric chloride than by an equal excess of stannous chloride.

---

* Zeit. phys. Chem., 16, 546 (1895).

Reactions of Higher Orders. Reactions of the fourth, fifth and eighth orders have recently been investigated, but examples of reactions of orders higher than the third are extremely rare. This fact is at first sight surprising since the equations of many chemical reactions involve a large number of molecules, and we would naturally expect the order of such reactions to be correspondingly high. For example, the reaction represented by the equation,

$$2\,PH_3 + 4\,O_2 = P_2O_5 + 3\,H_2O,$$

involves six molecules of the substances initially present and, therefore, we should infer it to be a reaction of the sixth order.

Kinetic experiments by van der Stadt have shown it to be a bimolecular reaction, the velocity of reaction being proportional to the concentrations of the phosphine and the oxygen. On allowing the gases to mix slowly by diffusion, it was discovered that the reaction actually takes place in several successive stages, the first stage being represented by the equation of the bimolecular reaction

$$PH_3 + O_2 = HPO_2 + H_2.$$

The subsequent changes, involving the oxidation of the products of this reaction, take place with great rapidity. It is highly probable that the equations which are ordinarily employed to represent chemical reactions really represent only the initial and final stages of a series of relatively simple reactions. Larmor[*] has shown that when chemical reactions are considered from the molecular standpoint, the bimolecular reaction is the most probable. He says, "Imagine a substance, say gaseous for simplicity, formed by the immediate spontaneous combination of three gaseous components A, B, and C. When these gases are mixed, the chances are very remote of the occurrence of the simultaneous triple encounter of an A, a B, and a C, which would be necessary to the immediate formation of an ABC; whereas if ever formed, it would be liable to the normal chance of dissociating by collisions; it would thus be practically non-existent in the statistical sense. But if an intermediate combination AB could exist, very transiently, though long enough to cover a considerable fraction of the

[*] Proc. Manchester Phil. Soc., 1908.

mean free path of the molecules, this will readily be formed by ordinary binary encounters of A and B, and another binary encounter of AB with C will now form the triple compound ABC in quantity."

Determination of the Order of a Reaction. It has been shown in the foregoing pages that the time required to complete a certain fraction of a reaction is dependent upon the order of the reaction in the following manner: —

(1) In a unimolecular reaction the value of k is independent of the initial concentration;

(2) In a bimolecular reaction the value of k is inversely proportional to the initial concentration;

(3) In a trimolecular reaction the value of k is inversely proportional to the square of the initial concentration.

Hence, in general, in a reaction of the nth. order, the value of k is inversely proportional to the $(n-1)$ power of the initial concentration. If the value of k is determined with definite concentrations of the reacting substances, and then with multiples of those concentrations, the order of the reaction can be determined according to the above rules by observing the manner in which k varies with the concentration.

The order of a reaction may also be readily determined by means of a graphic method. Thus, to determine the order of a reaction we ascertain by actual trial which one of the following expressions, in which C denotes concentration, will give a straight line when plotted against times as abscissæ: —

(1) $\log C$ — reaction unimolecular;
(2) $1/C$ — reaction bimolecular;
(3) $1/C^2$ — reaction trimolecular;
(4) $1/C^n$ — reaction $n+1$ molecular.

Complex Reaction Velocities. Thus far we have considered the velocity of reactions which are practically complete. There are numerous cases, however, in which the course of the reaction is complicated by such disturbing factors as (1) *counter reactions*, (2) *side reactions*, and (3) *consecutive reactions*. These disturbing causes will now be considered.

(1) *Counter Reactions.* In the chemical change represented by the equation

$$CH_3COOH + C_2H_5OH \rightleftarrows CH_3COOC_2H_5 + H_2O,$$

the speed of the direct reaction steadily diminishes owing to the ever-increasing effect of the reverse or counter reaction. Ultimately, when two-thirds of the acid and alcohol are decomposed, the velocities of the two reactions become equal and a condition of equilibrium results. Starting with 1 mol of acid and 1 mol of alcohol, and letting x represent the amount of ester formed, we have

$$\frac{dx}{dt} = k(1 - x)^2 - k'x^2 \cdot$$

When equilibrium is attained,

$$K_c = \frac{k}{k'} = 4 \cdot$$

By observing the change for any time t, we have

$$k - k' = \frac{3}{4t} \log_e \frac{2 - x}{2 - 3x} \cdot$$

Having the values of k/k' and $k - k'$, the velocity constant k of the direct reaction can be determined. The value of k so obtained has been shown by Knoblauch * to vary in those reactions where the concentration of the hydrogen ion changes.

(2) *Side Reactions.* When the same substances are capable of reacting in more than one way with the formation of different products, the several reactions proceed side by side. Thus, benzene and chlorine may react in two ways as shown by the equations,

$$(1) \quad C_6H_6 + Cl_2 = C_6H_5Cl + HCl$$

and

$$(2) \quad C_6H_6 + 3\,Cl_2 = C_6H_6Cl_6.$$

It is generally possible to regulate the conditions under which the substances react so as to produce one reaction and retard the other.

---

* Zeit. phys. Chem., 22, 268 (1897).

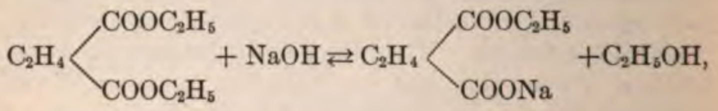
(3) *Consecutive Reactions.* By consecutive reactions we understand those reactions in which the products of a certain initial chemical change react, either with each other or with the original substances to form new substances. Attention has already been called to the fact that many of our common chemical equations really represent the summation of a number of consecutive reactions. If the system A is transformed into the system C through an intermediate system B, then we shall have the two reactions

$$(1) \quad A \rightarrow B,$$

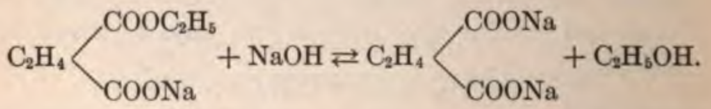
and

$$(2) \quad B \rightarrow C.$$

If reaction (1) should have a very much greater velocity than reaction (2), then the measured velocity of the change from A to C will be practically the same as that of the slower reaction. This fact has been illustrated by means of the following analogy, due to James Walker:—* "The time occupied by the transmission of a telegraphic message depends both on the rate of transmission along the conducting wire, and on the rate of progress of the messenger who delivers the telegram; but it is obviously this last, slower rate that is of really practical importance in determining the time of transmission." The saponification of ethyl succinate may be taken as an illustration of consecutive reactions. This reaction proceeds in two stages as follows:—

(1) 

$$(1) \quad C_2H_4\left\langle\begin{matrix}COOC_2H_5\\ COOC_2H_5\end{matrix}\right. + NaOH \rightleftarrows C_2H_4\left\langle\begin{matrix}COOC_2H_5\\ COONa\end{matrix}\right. + C_2H_5OH,$$

(2) 

$$(2) \quad C_2H_4\left\langle\begin{matrix}COOC_2H_5\\ COONa\end{matrix}\right. + NaOH \rightleftarrows C_2H_4\left\langle\begin{matrix}COONa\\ COONa\end{matrix}\right. + C_2H_5OH.$$

In this case the product of the first reaction reacts with one of the original substances.

Velocity of Heterogeneous Reactions. It has been shown that when a solid, such as calcium carbonate, is dissolved in an acid, the rate of solution is dependent upon the surface of contact between the solid and liquid phases, and also upon the strength of the acid. If the surface is large so that it undergoes relatively little change during the reaction, it may be considered as constant. If S represents the area of the surface exposed and x denotes the amount of solid dissolved in the time t, the velocity of the reaction will be represented by the differential equation

---

* Proc. Roy. Soc., Edinburgh, **22** (1898).

$$\frac{dx}{dt} = kS\,(a - x).$$

Integrating this equation, we have

$$kS = \frac{1}{t}\log_e \frac{a}{a - x}.$$

This formula has been tested by Boguski [*] for the reaction

$$CaCO_3 + 2\,HCl = CaCl_2 + CO_2 + H_2O,$$

and is found to give constant values of k. Furthermore, Noyes and Whitney [†] have shown that the rate of solution of a solid in a liquid at any instant, is proportional to the difference between the concentration of the saturated solution and the concentration of the solution at the time of the experiment.

Velocity of Reaction and Temperature. It is a well-established fact that the velocity of a chemical reaction is accelerated by rise of temperature. Thus, the rate of inversion of cane sugar is increased about five times for a rise in temperature of 30°. It has been shown as the result of a large number of observations on a variety of chemical reactions, that in general the velocity of a reaction is doubled or trebled for an increase in temperature of 10°. It is of interest to note that the rate of development of various organisms, such as yeast cells, the rate of growth of the eggs of certain fishes, and the rate of germination of certain varieties of seeds is either doubled or trebled for a rise in temperature of 10°. Up to the present time no wholly satisfactory formula, connecting the rate of reaction with the temperature, has been derived, although several purely-empirical expressions have been suggested. Of these formulas the most widely applicable is that proposed by van't Hoff and verified by Arrhenius. If k_0 and k_1 represent the velocity constants at the respective temperatures T_0 and T_1, then

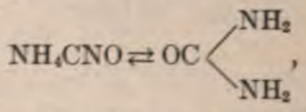
---

[*] Berichte, **9**, 1646 (1876).

[†] Zeit. phys. Chem., **23**, 689 (1897).

$$k_1 = k_0 e^{\left(\frac{A\,(T_1 - T_0)}{T_0 T_1}\right)},$$

where e is the base of the Naperian system of logarithms and A is a constant. The following table gives the calculated and observed values of k at various temperatures for the reaction



$$NH_4CNO \rightleftarrows OC\begin{matrix} NH_2 \\ NH_2 \end{matrix},$$

when $T = 273° + 25°$, $k = 0.000227$ and $A = 11{,}700$.

T, Degrees	K (observed).	k (calculated).
273 + 39	0.00141	0.00133
273 + 50.1	0.00520	0.00480
273 + 64.5	0.0228	0.0227
273 + 74.7	0.062	0.0623
273 + 80	0.100	0.105

In this case the agreement between the observed and calculated values is all that could be desired.

Influence of the Solvent on the Velocity of Reaction. The velocity of a chemical reaction varies greatly with the nature of the medium in which it takes place. This subject has been studied by Menschutkin * who has collected much valuable data, as the result of a large number of experiments, on the velocity of the reaction between ethyl iodide and triethylamine, as represented by the equation

$$C_2H_5I + (C_2H_5)_3N = (C_2H_5)_4NI.$$

This reaction was allowed to take place in a large number of different solvents and the velocity at 100° was measured. A few of Menschutkin's results are given in the accompanying table, in which k denotes the velocity constant: —

---

* Zeit. phys. Chem., **6**, 41 (1890).

Medium.	k	Medium.	k
Hexane	0.00018	Ethyl alcohol	0.0366
Ethylether	0.000757	Methyl alcohol	0.0516
Benzene	0.00584	Acetone	0.0608

These figures show that the velocity of the reaction is greatly modified by the nature of the medium in which it takes place, the velocity in hexane being less than one three-hundredth of that in acetone. It is of interest to note that there is an approximate parallelism between the values of k, and the values of the dielectric constant of the different media.

Catalysis. It is a familiar fact that the velocity of reaction is frequently greatly accelerated by the presence of a foreign substance which apparently does not participate in the reaction, and which remains unchanged when the reaction is complete. For example, cane sugar is inverted very slowly by pure water alone, but when a trace of acid is added the reaction is greatly accelerated. A substance which is capable of exerting such an accelerating action is termed a *catalyst*, and the process is known as *catalysis*. In addition to the fact that a relatively-small amount of a catalyst is capable of effecting the transformation of large amounts of material, there are two other important characteristics of catalytic action which should be mentioned: *viz.*, (*a*) a catalyst does not initiate a reaction but simply promotes it; and (*b*) the equilibrium is not disturbed by the presence of a catalyst, since the velocities of the direct and reverse reactions are each altered to the same extent. As the result of a series of experiments, Ostwald concludes that the catalytic effect of acids in hastening the inversion of cane sugar is directly proportional to the concentration of the hydrogen ion, and, in general, is independent of the nature of the anion. Similarly, the catalytic action of bases may be attributed to the hydroxyl ion, the effect being proportional to the concentration of this ion. In fact we may formulate the following fundamental law of catalysis: — *The degree of catalytic action is directly proportional to the concentration of the catalytic agent.* Almost every chemical reaction can be accelerated by the addition of an appropriate catalyst. A few typical reactions which are accelerated catalytically are here given, together with the catalyst employed: —

Catalyst — hydrogen ion,

$$CH_3COOC_2H_5 + H_2O = CH_3COOH + C_2H_5OH,$$

Catalyst — hydroxyl ion,

$$2\,CH_3{\cdot}CO{\cdot}CH_3 = CH_3{\cdot}CO{\cdot}CH_2C(CH_3)_2OH,$$

Catalyst — finely divided platinum,

$$2\,SO_2 + O_2 = 2\,SO_3,$$

$$2\,CH_3OH + O_2 = 2\,H{\cdot}COH + 2\,H_2O,$$

$$2\,H_2 + O_2 = 2\,H_2O,$$

Catalyst — water vapor,

$$2\,CO + O_2 = 2\,CO_2,$$

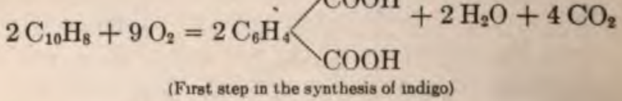
$$NH_4Cl = NH_3 + HCl,$$

Catalyst — copper sulphate,

$$4\,HCl + O_2 = 2\,H_2O + 2\,Cl_2,$$

(Deacon Process)

Catalyst — mercury salts,



$$2\,C_{10}H_8 + 9\,O_2 = 2\,C_6H_4\begin{matrix}\diagup COOH\\ \diagdown COOH\end{matrix} + 2\,H_2O + 4\,CO_2$$

(First step in the synthesis of indigo)

Catalyst — colloidal platinum,

$$2\,H_2O_2 = 2\,H_2O + O_2,$$

Catalyst — enzymes,

$$C_6H_{12}O_6 = 2\,C_2H_5OH + 2\,CO_2,$$

(zymase)

$$C_3H_7COOH + C_2H_3OH = C_3H_7COOC_2H_5 + H_2O.$$

(lipase)

It will be seen that catalysis is of great importance in connection with many industrial processes as well as in the field of pure chemistry. The majority of the reactions occurring within living organisms are accelerated catalytically by unorganized ferments or enzymes. Thus, before the process of digestion can proceed, starch must be changed into sugar. This transformation is accelerated by an enzyme called ptyalin occurring in the saliva, and by other enzymes found in the pancreatic juice. The digestion of albumen is hastened by the enzymes, pepsin and trypsin. As a rule each enzyme acts catalytically on just one reaction, or in other words the catalytic action of enzymes is specific. Enzymes are very sensitive to traces of certain toxic substances such as hydrocyanic acid, iodine, and mercuric chloride.

An interesting series of experiments by Bredig * on the catalytic action of colloidal metals, established the fact that these substances resemble the enzymes very closely in their behavior. Thus, they are "poisoned" by the same substances which inhibit the activity of the enzymes, and they show the same tendency to recover when the amount of the poison does not exceed a certain limiting value. Because of this close similarity, Bredig called the colloidal metals *inorganic ferments.*

It sometimes happens that one of the products of a chemical reaction functions as a catalyst to the reaction. Thus, when metallic copper is dissolved in nitric acid, the reaction proceeds slowly at first and then, after a short interval, the speed of the reaction is greatly augmented. The acceleration is due to the catalytic action of the nitric oxide evolved. This phenomenon is known as *autocatalysis.* In reactions where autocatalysis occurs, the velocity increases with the time until a certain maximum value is reached, after which the velocity steadily diminishes. In ordinary reactions the initial velocity is the greatest.

It sometimes happens that the speed of a reaction is retarded by the presence of a trace of some foreign substance. Thus, Bigelow † has shown that the rate of oxidation of sodium sulphite is retarded by the presence in the solution of only one one-hundred-

---

* Zeit. phys. Chem., 31, 258 (1899).

† Zeit. phys. Chem., 26, 493 (1898).

and-sixty-thousandth of a formula weight of mannite per liter. Such a substance is termed a *negative catalyst.*

Mechanism of Catalysis. As to the cause of catalytic action very little is known. In fact it is more reasonable to suppose that the mechanism of catalysis varies with the nature of the reaction and the nature of the catalyst, than to conceive all catalytic effects to be traceable to a common origin. One of the earliest hypotheses as to the mechanism of catalysis was put forward by Liebig. He suggested that the catalyst sets up intramolecular vibrations which assist chemical reaction. The vibration theory was gradually abandoned as its inadequacy came to be recognized. Of the many explanations which have been offered to account for catalytic acceleration, that involving the formation of hypothetical intermediate compounds with the catalyst has been accepted with the greatest favor. Thus, if a reaction represented by the equation

$$A + B = AB,$$

takes place very slowly under ordinary conditions, it is possible to accelerate its velocity by the addition of an appropriate catalyst C. According to the theory of intermediate compounds, the catalyst is supposed to act in the following manner: —

$$(1)\quad A + C = AC,$$
$$(2)\quad AC + B = AB + C.$$

As will be seen, the catalyst is regenerated in the second stage of the reaction. In 1806 Clement and Desormes suggested that the action of nitric oxide in promoting the oxidation of sulphur dioxide in the manufacture of sulphuric acid was purely catalytic. As is well known, the rate of the reaction represented by the equation

$$2\,SO_2 + O_2 = 2\,SO_3,$$

is very slow. The accelerating action of nitric oxide on the reaction may be represented in the following manner: —

$$(1)\quad 2\,NO + O_2 = 2\,NO_2,$$

and

$$(2)\quad SO_2 + NO_2 = SO_3 + NO.$$

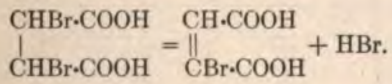
This explanation, first offered by Clement and Desormes, is still regarded as the most plausible explanation of the part played by the oxides of nitrogen in the synthesis of sulphuric acid. It is apparent that this so-called explanation is far from complete. In fact, it must be admitted that we have no adequate explanation of the phenomenon of catalysis. When we are able to answer the question — "Why does a chemical reaction take place?"— then we may be able to explain the accelerating and retarding influences of certain foreign substances on the speed of reactions. Ostwald likens the action of a catalyst to that of a lubricant on a machine — it helps to overcome the resistance of the reaction. If the velocity of a reaction is represented by an equation similar to that expressing Ohm's law, we have

$$\text{velocity of reaction} = \frac{\text{driving force}}{\text{resistance}}.$$

The driving force is the same thing as the free energy or chemical affinity of the reacting substances; of the resistance we know practically nothing. The velocity, according to the above expression, can be increased in either of two ways, *viz.*, (1) by increasing the driving force, or (2) by diminishing the resistance. It is inconceivable that a catalyst can exert any effect upon the chemical affinity of the reacting substances, so that we are forced to conclude that its action must be confined to lessening the resistance.*

PROBLEMS.

1. When a solution of dibromsuccinic acid is heated, the acid decomposes into brom-maleic acid and hydrobromic acid according to the equation



$$\begin{array}{l}\mathrm{CHBr\cdot COOH}\\ |\\ \mathrm{CHBr\cdot COOH}\end{array} = \begin{array}{l}\mathrm{CH\cdot COOH}\\ \|\\ \mathrm{CBr\cdot COOH}\end{array} + \mathrm{HBr}.$$

---

* For an excellent review of the subject of catalysis the student is advised to consult "Die Lehre von der Reaktionsbeschleunigung durch Fremdstoffe," by W. Herz. Ahrens' "Sammlung chemischer and chemisch-technischer Vortraege."

At 50° the initial titre of a definite volume of the solution was $T_0 =$ 10.095 cc. of standard alkali. After t minutes the titre of the same volume of solution was T_t cc. of standard alkali.

t	0	214	380
T_t	10.095	10.37	10.57

(a) Calculate the velocity-constant of the reaction.

(b) After what time is one-third of the dibromsuccinic acid decomposed? *Ans.* (a) 0.000260; (b) 1559 minutes.

2. From the following data show that the decomposition of H_2O_2 in aqueous solution is a unimolecular reaction: —

Time in minutes	0	10	20
n	22.8	13.8	8.25 cc.

n is the number of cubic centimeters of potassium permanganate required to decompose a definite volume of the hydrogen peroxide solution.

3. In the saponification of ethyl acetate by sodium hydroxide at 10°, y cc. of 0.043 molar hydrochloric acid were required to neutralize 100 cc. of the reaction mixture t minutes after the commencement of the reaction.

t	0	4.89	10.37	28.18	infinity
y	61.95	50.59	42.40	29.35	14.92

Calculate the velocity-constant when the concentrations are expressed in mols per liter. *Ans.* Mean value of $k = 2.38$.

4. The velocity-constant of formation of hydriodic acid from its elements is 0.00023; the equilibrium constant at the same temperature is 0.0157. What is the velocity-constant of the reverse reaction? *Ans.* 0.0146.

5. Determine the order of the following reaction: —

$$6\,FeCl_2 + KClO_3 + 6\,HCl = 6\,FeCl_3 + KCl + 3\,H_2O.$$

When the initial concentration of the reacting substances is 0.1, the changes in concentration at successive times are as follows: —

Time (minutes).	Change in Concentration.
5	0.0048
15	0.0122
35	0.0238
60	0.0329
110	0.0452
170	0.0525

Ans. Third order.

CHAPTER XVIII.

ELECTRICAL CONDUCTANCE.

Historical Introduction. In a book of this character it is impossible to give anything like a complete historical sketch of electrochemistry. Before entering upon an outline of this interesting division of theoretical chemistry, however, it is desirable to consider very briefly a few of the theories which have played a prominent part in the development of our modern views concerning electrochemical phenomena. While the early observations of Beccaria and others pointed to the probability of the existence of some relation between chemical and electrical phenomena, it was not until the beginning of the nineteenth century that the science of electrochemistry had its birth. The epoch-making discovery by Volta of a means of obtaining electrical energy from chemical energy, gave the initial impulse to all the brilliant discoveries and investigations upon which the modern science of electrochemistry is based. The apparatus devised by Volta, known as the *voltaic pile*, consisted of disks of zinc and silver placed alternately over one another, the silver disk of one pair being separated from the zinc disk of the next by a piece of blotting paper moistened with brine. Such a pile, if composed of a sufficient number of pairs of disks, will produce electricity enough to give a shock, if the top and bottom disks, or wires connected with them, be touched with the moist fingers. This discovery placed in the hands of the investigator a source of electricity by means of which experiments could be performed which had hitherto been impossible. Shortly after the discovery of the voltaic pile, Nicholson and Carlisle * effected the decomposition of water, and Davy † isolated the alkali metals. As a result of these experiments, Davy was led to formulate his electrochemical theory. According to this theory, the atoms of different substances acquire opposite electrical charges by contact, and thus mutually attract each other. If the differences between the charges are small, the attraction will be insufficient to cause the atoms to leave their former positions; if it is great, a rearrangement of the atoms will occur and a chemical compound will be formed. In terms of this theory, electrolysis consists in a neutralization of the charges upon the atoms.

---

* Nich. Jour., **4**, 179 (1800).

† Ibid., **4**, 275, 326 (1800); Gilb. Ann., **7**, 114 (1801).

The theory of Davy was soon superseded by that of Berzelius.* According to the latter theory, every atom is charged with both kinds of electricity which exist upon the atoms in a polar arrangement, the electrical behavior of the atom being determined by the kind of electricity which is in excess. Chemical attraction is merely the electrical attraction of oppositely-charged atoms. Since each atom is endowed with both positive and negative electrification, one charge being in excess, it follows that the compound formed by the union of two or more atoms will be positively or negatively charged according to whichever charge remains unneutralized after the atoms have combined. Two compounds, the one charged positively and the other negatively, may thus in turn combine, a more complex compound being formed. Shortly after Berzelius formulated his theory, it became the subject of much discussion and was severely criticized. Thus, it was pointed out that if chemical combination results from the neutralization of oppositely-charged atoms, then as soon as the charges have become equalized, there no longer exists any attractive force and the compound must again decompose. This objection was easily overcome by assuming that as soon as the union between the atoms is broken, they again acquire their original charges and, in consequence, recombine. In other words, a chemical compound is to be regarded as existing in a state of unstable equilibrium. Another, and apparently insurmountable, objection to the theory resulted from the exceptions presented by acetic acid and some of its substitution products.

According to the theory of Berzelius, chemical combination is entirely dependent upon the nature of the electrical charges residing on the atoms. From this statement it follows that the properties of a chemical compound must be a function of the electrical charges upon the atoms of its constituents. It was shown that when the three hydrogen atoms of the methyl group in acetic acid are successively replaced by chlorine, the chemical properties of the original substance are not materially altered. According to Berzelius, the three hydrogen atoms are positively charged while the three chlorine atoms are negatively charged. That three negative charges could be substituted for three positive charges in acetic acid without producing a more marked change in its properties, could not be satisfactorily accounted for by the theory. This criticism was for a long time considered as an insuperable barrier to the acceptance of the theory. Shortly before the close of the nineteenth century, J. J. Thomson * showed that this objection has little or no weight. When hydrogen gas is electrolyzed in a vacuum-tube and the spectra at the two electrodes are compared, Thomson found them to differ widely. From this he concluded that the molecule of hydrogen gas is in all probability made up of positively- and negatively-charged parts or ions. He then extended his experiments to the vapors of certain organic compounds. In discussing these experiments he says: — "In many organic compounds, atoms of an electropositive element, hydrogen, are replaced by atoms of an electronegative element, chlorine, without altering the type of the compound. Thus, for example, we can replace the four hydrogen atoms in CH_4 by chlorine atoms, getting, successively, the compounds CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4. It seemed of interest to investigate what was the nature of the charge of electricity on the chlorine atoms in these compounds. The point is of some historical interest, as the possibility of substituting an electronegative element in a compound for an electropositive one was one of the chief objections against the electrochemical theory of Berzelius."

---

* Gilb. Ann., 27, 270 (1807).

"When the vapor of chloroform was placed in the tube, it was found that both the hydrogen and chlorine lines were bright on the negative side of the plate, while they were absent from the

---

* Nature, **52**, 451 (1895).

positive side, and that any increase in brightness of the hydrogen lines was accompanied by an increase in the brightness of those due to chlorine. The appearance of the hydrogen and chlorine spectra on the same side of the plate was also observed in methylene chloride and in ethylene chloride. Even when all the hydrogen in methane was replaced by chlorine, as in carbon tetrachloride, the chlorine spectra still clung to the negative side of the plate. The same point was tested with silicon tetrachloride and the chlorine spectrum was brightest on the negative side of the plate. From these experiments it would appear, that the chlorine atoms in the chlorine derivatives of methane are charged with electricity of the same sign as the hydrogen atoms they displace."

Electrical Units. In 1827, Dr. G. S. Ohm enunciated his well-known law of electrical conductance, *viz.:— The strength of the electric current flowing in a conductor is directly proportional to the difference of potential between the ends of the conductor, and inversely proportional to its resistance.* If C represents the strength of the current, E the difference of potential, and R the resistance, then Ohm's law may be formulated thus:—

$$C = \frac{E}{R}.$$

The unit of resistance is the *ohm*, that of difference of potential or electromotive force, the *volt*, and that of current, the *ampere*. The ohm is defined as the resistance of a column of mercury 106.3 cm. long and 1 sq. mm. in cross section at 0° C. The ampere is defined as the current which will cause the deposition of 0.001118 gram of silver from a solution of silver nitrate in 1 second. The volt may be defined as the electromotive force necessary to drive a current of 1 ampere through a resistance of 1 ohm. The unit of quantity of electricity is the *coulomb*, and is equivalent to a current of 1 ampere per second. One gram equivalent of any ion carries 96,500 coulombs, a quantity of electricity known as the *faraday* = F. As has already been pointed out, any form of energy may be considered as the product of two factors, a capacity factor and an intensity factor.

The capacity factor of electrical energy is the coulomb while the intensity factor is the volt, *i.e.*,

$$\text{electrical energy} = \text{coulombs} \times \text{volts.}$$

The unit of electrical energy, therefore, is the *volt-ampere-second* commonly called the *watt-second.* One watt-second is the electrical work done by a current of 1 ampere flowing under an electromotive force of 1 volt for 1 second, and is equivalent to 1×10^7 C.G.S. units. The thermal equivalent of electrical energy may be calculated from the relation

$$\frac{\text{electrical energy in absolute units}}{\text{mechanical equiv. of heat}} = \text{heat equiv. of elect. energy,}$$

or

$$\frac{1 \times 10^7}{42{,}600 \times 980.1} = 0.2394 \text{ cal.} = 1 \text{ watt-second.}$$

Faraday's Laws. When two platinum plates or electrodes, one connected to the positive and the other to the negative terminal of a battery, are immersed in a solution of sodium chloride, it will be found that hydrogen is immediately evolved at the negative electrode and oxygen at the positive electrode. If the salt solution is previously colored with a few drops of a solution of litmus it will be observed that the portion of the solution in the neighborhood of the positive electrode will turn red, indicating the formation of an acid, while that in the neighborhood of the negative electrode will turn blue, showing the formation of a base. The same changes will take place whether the electrodes are placed near together or far apart, and furthermore, the evolution of gas and the change in color at the electrodes commences as soon as the circuit is closed. The study of these phenomena led Faraday * to the conclusion, that when an electric current traverses a solution, there occurs an actual transfer of matter, one portion travelling with the current and the other portion moving in the opposite direction. At the suggestion of the philologist Whewell, Faraday termed these carriers of the current, *ions* (ἰέναι = to wander). He also called the electrode connected to

---

[*] Experimental Researches, (1834).

the positive terminal of the battery, the *anode*, (ἀνά = up and ὁδός = way), and the electrode connected to the negative terminal the *cathode*, (κατά = down and ὁδός = way). The ions which move toward the anode he called *anions*, while those which migrate toward the cathode he called *cations*. The whole process he termed *electrolysis*. The question of the relationship between the amount of electrolysis and the quantity of electricity passing through a solution was investigated by Faraday. As a result of his experiments he enunciated the following laws which are commonly known as the laws of Faraday: —

(1) *For the same electrolyte, the amount of electrolysis is proportional to the quantity of electricity which passes.*

(2) *The amounts of substances liberated at the electrodes when the same quantity of electricity passes through solutions of different electrolytes, are proportional to their chemical equivalents.* The *chemical equivalent* of any ion is equal to the atomic weight divided by its valence. If the same quantity of electricity is passed through solutions of hydrochloric acid, silver nitrate, cuprous chloride, cupric chloride, and auric chloride, the relative amounts of the different cations liberated will be as follows: —

Electrolyte.	Chem. Equiv. of Cation.
HCl	$H^{\cdot} = 1$
$AgNO_3$	$Ag^{\cdot} = 108$
Cu_2Cl_2	$Cu^{\cdot} = 63.4$
$CuCl_2$	$Cu^{\cdot\cdot} = 63.4 \div 2$
$AuCl_3$	$Au^{\cdot\cdot\cdot} = 197 \div 3$

The *electrochemical equivalent* of an element or group of elements is the weight in grams which is liberated by the passage of one coulomb of electricity. The electrochemical equivalents are, according to Faraday's second law, proportional to the chemical equivalents. The quantity of electricity necessary to liberate one chemical equivalent in grams is called a *faraday*. This is a very important unit in electrochemical calculations. Since one coulomb liberates 0.00001036 gram of hydrogen, 1 ÷ 0.00001036 = 96,500 coulombs of electricity will be required to liberate one gram equivalent of hydrogen. The same quantity of electricity will liberate $35.45 \times 0.00001036 = 0.000368$ gram of chlorine, and $108 \times 0.00001036 = 0.001118$ gram of silver. Or, in general, since one coulomb of electricity liberates 0.00001036 gram of hydrogen, it will cause the liberation of $0.00001036\ w$ grams of any other element whose equivalent weight is w.

The Existence of Free Ions. When an electrolyte is decomposed by the electric current, the products of decomposition appear at the electrodes. The fact that the liberation of the products of decomposition is independent of the distance between the electrodes caused considerable difficulty in the early history of electrolysis. It was evident that the two products could hardly be derived from the same molecule, but must come from two different molecules. Several theories were advanced to account for the experimental results. Thus, in the electrolysis of water it was suggested that the two gases, hydrogen and oxygen, were not derived from the water but that electricity itself possessed an acid character. Grotthuss * was the first to propose a rational hypothesis as to the mechanism of electrolysis. He assumed that when the electrodes in an electrolytic cell are connected with a source of electricity, the molecules of the electrolyte arrange themselves in straight lines between the electrodes, the positive poles being directed toward the negative electrode and the negative poles toward the positive electrode. When electrolysis begins, the cation of the molecule nearest the cathode is liberated at the cathode and the anion of the molecule nearest the anode is liberated at the anode. The anion which is left free near the cathode then combines with the cation of the next adjoining molecule, the anion thus left uncombined uniting with the cation of its nearest neighbor, a similar exchange of partners continuing throughout the entire molecular chain. Under the directive influence of the two electrodes, the newly-grouped molecules then rotate so that the positive poles all face the negative electrode and the negative poles all face the positive electrode. The process is then repeated, another molecule being electrolyzed.

---

* Ann. de Chim. [1], 58, 54 (1806).

This theory of electrolysis appears to have been accepted by Faraday. Its inherent defect was first pointed out by Grove.[*] From his experiments with the oxy-hydrogen cell, which derives its energy from the union of hydrogen and oxygen, he pointed out that a decomposition of the molecules of water is not essential for the evolution of these two gases, but that the molecules must be already in a state of partial decomposition. This suggestion was followed up by Clausius.[†] He argued that if an expenditure of energy is necessary to decompose the molecules, electrolysis should be impossible at very low voltages. Experiment showed that when silver nitrate is electrolyzed between silver electrodes, decomposition takes place at voltages which are much below the voltage corresponding to the energy of formation of silver nitrate. In other words, it requires very little energy to decompose a salt which is formed with the evolution of a large amount of energy, a result which is in contradiction to the principle of the conservation of energy. Clausius was thus forced to conclude "that the supposition that the constituents of the molecule of an electrolyte are firmly united and exist in a fixed and orderly arrangement is wholly erroneous."

As a result of his investigation of the synthesis of ethyl ether from alcohol and sulphuric acid, Williamson[‡] concluded "that in an aggregate of the molecules of every compound, a constant interchange between the elements contained in them is taking place." In the same paper he writes, "each atom of hydrogen does not remain quietly attached all the time to the same atom of chlorine, but they are continually exchanging places with one another." This view was accepted by Clausius, although he had no means of determining the extent to which the electrolyte was broken down or dissociated into free ions.

In 1887, Arrhenius[§] developed the views of Clausius by showing how the degree of dissociation of the molecules of an electrolyte can be deduced from measurements of the electrical conductance of its solutions, as well as from measurements of osmotic pressure and freezing-point lowering. The important generalization summarizing these conceptions is known as the theory of electrolytic dissociation, to which reference has already been made in earlier chapters (see page 227).

---

[*] Phil. Mag., 27, 348 (1845).

[†] Pogg. Ann., 101, 338 (1857).

[‡] Lieb. Ann., 77, 37 (1851).

[§] Zeit. phys. Chem., 1, 631 (1887).

The Migration of the Ions. Since the passage of a current of electricity through a solution of an electrolyte causes the discharge of equivalent amounts of positive and negative ions at the electrodes, it might be inferred that the ions all move with the same speed. That this inference is incorrect, was first shown by Hittorf[*] as the result of his observations on the changes in concentration of the solution in the neighborhood of the electrodes during electrolysis. He showed that different ions migrate with different speeds, and that the faster moving ions carry a greater proportion of the current than the slower moving ions. The effect of unequal ionic velocities on the concentrations of the solutions around the electrodes is clearly shown by the accompanying diagram (Fig. 87) due to Ostwald. The anode and

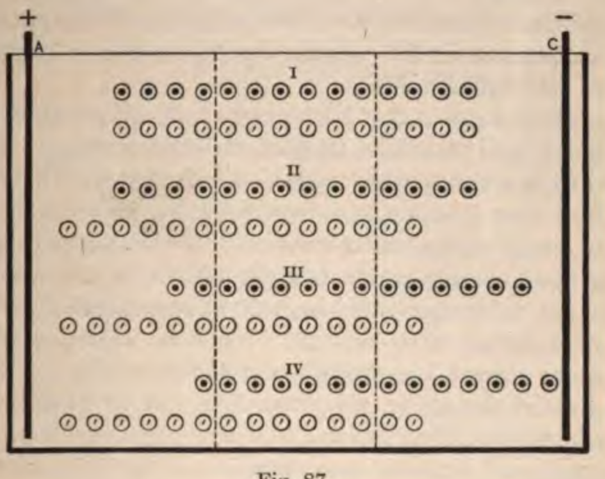


Fig. 87.

---

[*] Pogg. Ann., 89, 177; 98, 1; 103, 1; 106, 337, 513 (1853–1859).

cathode in an electrolytic cell are represented by the vertical lines *A* and *C* respectively. The cell is divided into three compartments by means of porous diaphragms, represented by the vertical dotted lines. The cations are represented by dots (˙) and the anions by dashes (′). Before the current passes through the cell, the concentration of the solution is uniform throughout, the conditions being represented by I. Now let us imagine that only the anions move when the current is established. The conditions when the chain of anions has moved two steps toward the anode are shown in II. Each ion which has been deprived of a partner is supposed to be discharged. It will be observed that although the cations have not migrated toward the cathode, yet an equal number of positive and negative ions are discharged, and that while the concentration in the anode compartment has not changed, the concentration in the cathode compartment has diminished to one-half its original value.

Let us now suppose that both anions and cations move with the same speed, and as before, let each chain of ions move two steps toward their respective electrodes, as indicated in III. It will be seen that four positive and four negative ions have been discharged, and that the concentration of the electrolyte in the anode and cathode compartments has diminished to the same extent. Finally, let us assume that the ratio of the speeds of the cations to that of the anions is as 3 : 2. When the cations have moved three steps toward the cathode and the anions have moved two steps toward the anode, the conditions will be as shown in IV. It is evident that five positive and five negative ions have been discharged, and that the concentration in the cathode compartment has diminished by two molecules while the concentration in the anode compartment has diminished by three molecules. It will be observed that the change in concentration in either of the electrode compartments is proportional to the speed of the ion leaving it. Thus, in II, the concentration in the cathode compartment diminishes while that in the anode compartment remains unchanged, since only the anion moves. In like manner, the change in concentration about the electrodes in III corresponds with the fact that both ions migrate at the same rate.

In IV the ratio of the change in concentration in the cathode compartment to that in the anode compartment is as 2 : 3. It will be apparent from these examples, that the relation between the speeds of the ions and the corresponding changes in concentration at the electrodes may be expressed by the following proportion: —

$$\frac{\text{Change in concentration at anode}}{\text{Change in concentration at cathode}} = \frac{\text{speed of cation}}{\text{speed of anion}}.$$

If the relative speed of the cations is represented by u, and that of the anions by v, then the total quantity of electricity transported will be proportional to $u + v$: of this total, the fractions carried by the anion and cation respectively, will be $n = \frac{v}{u + v}$, and $1 - n = \frac{u}{u + v}$. The values of these ratios, n and $1 - n$, are called the *transport numbers* of the anion and cation respectively. It is apparent from the diagram, that if the electrolysis is not carried too far, the concentration of the solution in the intermediate compartment will undergo no change. In order to determine transport numbers, therefore, it is simply necessary to remove portions of the solutions in the immediate vicinity of the two electrodes and determine the concentration of the electrolyte analytically. The success of the experiment depends upon keeping the concentration of the intermediate compartment unaltered.

Experimental Determination of Transport Numbers. Various forms of apparatus have been constructed for the determination of transport numbers, among which one of the most satisfactory is that devised by Jones and Bassett,* and shown in Fig. 88. It consists of two vertical tubes of wide bore connected by a U-tube fitted with a stop-cock. Into each of two electrodes, made of a suitable metal, is riveted a short piece of stout platinum wire, which is then sealed into heavy-walled glass tubes. The exposed end of the platinum wire on the under side of each electrode is covered with a drop of fusion glass. The tubes carrying the electrodes are fitted into holes bored through the ground glass stoppers which close the right and left arms of the apparatus. Two small graduated tubes are sealed to the two vertical tubes just below the stoppers. These tubes allow for any slight displacement of the solution due to expansion or the formation of gas, and at the same time make it possible to level the apparatus accurately. When electrolysis has proceeded far enough, the circuit is broken and the stop-cock closed, thus preventing the mixing of the solutions in the anode and cathode compartments. The solutions in the two halves of the apparatus are then rinsed out into separate beakers and the concentration of each is determined analytically. Knowing the initial concentration of the solution and the final concentrations at the two electrodes, together with the total quantity of electricity which has passed through the apparatus during the experiment, we have all of the data necessary for the calculation of the transport numbers of the two ions.

---

* Am. Chem. Jour., 32, 409 (1904).

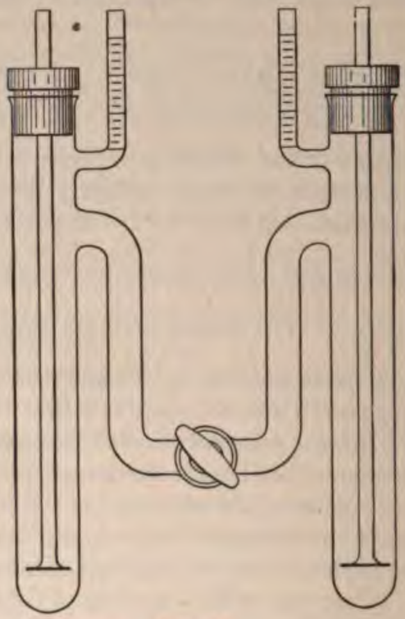


Fig. 88.

The following example will serve to make the method of calculation clear: — In an experiment to determine the transport numbers of the ions of silver nitrate, a solution containing 0.00739 gram of that salt per gram of water was prepared. The solution was introduced into the migration apparatus and, after inserting silver electrodes, a small current was passed through the apparatus for two hours. A silver coulometer was included in the circuit, and 0.0780 gram of silver was deposited by the current.

This mass of silver is equivalent to 0.000723 gram-equivalent. After the circuit was broken, the anode solution was rinsed out and its concentration determined analytically. It was found to contain 0.2361 gram of silver nitrate to 23.14 grams of water. This amount of solution contained originally $23.14 \times 0.00739 = 0.1710$ gram of silver nitrate. Thus, the amount of silver nitrate in the anode compartment had increased by $0.2361 - 0.1710 = 0.0651$ gram of silver nitrate, or 0.000383 gram-equivalent of silver. Obviously the increase in the concentration of the nitrate ion must have been the same. The amount of silver dissolved from the anode must have been equal to that deposited in the coulometer, or since 0.000723 gram-equivalent of silver was deposited and the actual increase found was 0.000383 gram-equivalent, the difference, $0.000723 - 0.000383 = 0.000340$ gram-equivalent, is the amount of silver which migrated away from the anode. At the same time 0.000383 gram-equivalent of nitrate ions migrated into the anode compartment. The ratio of the speed of migration of the silver ions to that of the nitrate ions is as 0.000340 : 0.000383. Since 0.000723 gram-equivalent of silver ions measures the total quantity of electricity transported, the transport numbers of the two ions will be as follows: —

$$\text{Transport number of } Ag^{\cdot} = n = \frac{0.000340}{0.000723} = 0.470,$$

$$\text{Transport number of } NO_3{}' = 1 - n = \frac{0.000383}{0.000723} = 0.530.$$

These numbers can be checked by a similar calculation based on the change in concentration in the cathode compartment.

The following table gives the transport numbers of the anions of various electrolytes at different dilutions, *V* being the number of liters of solution containing one gram-equivalent of solute. The transport numbers of the corresponding cations can be found by subtracting the transport numbers of the anions from unity.

TRANSPORT NUMBERS OF ANIONS.

V =	100	50	20	10	5	2	1	0.5
KCl KBr KI NH_4Cl	0.506	0.507	0.507	0.508	0.509	0.513	0.514	0.515
$NaCl$	....	....	0.614	0.617	0.620	0.626	0.637	....
KNO_3	....	....	....	0.497	0.496	0.492	0.487	0.479
$AgNO_3$	0.528	0.528	0.528	0.528	0.527	0.519	0.501	0.476
KOH	....	....	....	0.735	0.736	....	....	....
HCl	....	....	0.172	0.172	0.172	0.173	0.176	....
$\frac{1}{2}$ $BaCl_2$	....	....	....	....	....	....	0.640	0.657
$\frac{1}{2}$ K_2CO_3	....	....	....	....	....	0.435	0.434	0.413
$\frac{1}{2}$ $CuSO_4$	....	0.620	0.626	0.632	0.643	0.668	0.696	0.720
$\frac{1}{2}$ H_2SO_4	....	....	....	....	....	0.182	0.174	....

It is apparent from the table that the transport numbers are not entirely independent of the concentration. They also vary slightly with the temperature and approach the limiting value, 0.5, at high temperatures.

Specific, Molar and Equivalent Conductance. As is well known, the resistance of a metallic conductor is directly proportional to its length and inversely proportional to its area of cross-section. Similarly, the resistance of an electrolyte is proportional to the length and inversely proportional to the cross-section of the column of solution between the two electrodes. The *specific resistance* of an electrolyte may be defined as the resistance in ohms of a column of solution one centimeter long and one square centimeter in cross-section. *Specific conductance* is the reciprocal of specific resistance. Since the conductance of a solution is almost wholly dependent upon the amount of solute present, it is more convenient to express conductance in terms of the molar or equivalent concentration. The *molar conductance* μ, is the conductance in reciprocal ohms, of a solution containing one mol of solute when placed between electrodes which are exactly one centimeter apart. The *equivalent conductance* Λ is the conductance in reciprocal ohms of a solution containing one gram-equivalent of solute when placed between electrodes which are one centimeter apart. If κ denotes the specific conductance of a solution and V_m, the volume in cubic centimeters which contains one mol of solute, then

$$\mu = \kappa V_m,$$

and in like manner

$$\Lambda = \kappa V_e,$$

where V_e is the volume of solution in cubic centimeters which contains one gram-equivalent of solute. The following table gives the specific and molar conductance of solutions of sodium chloride at 18° C.: —

Concentration.	Dilution.	Sp. Cond.	Molar Cond.
1	1,000	0.0744	74.4
0.1	10,000	0.00925	92.5
0.01	100,000	0.001028	102.8
0.001	1,000,000	0.0001078	107.8
0.0001	10,000,000	0.00001097	109.7

It will be observed that the molar conductance increases with the dilution up to a certain point beyond which it remains nearly constant. That the molar conductance should change but little will become apparent from the following considerations: — Imagine a rectangular cell of indefinite height and having a cross-sectional area of one square centimeter, and further assume that two opposite walls can function as electrodes. Let 1000 cc. of a solution containing one mol of solute be introduced into the cell, and let its conductance be determined. Now let the solution be diluted to 2000 cc. and the conductance of the diluted solution be measured. While the specific conductance of the diluted solution is reduced to one-half of its original value, yet since the electrode surface in contact with the solution is doubled, owing to the fact that the solution stands at twice the original height in the cell, the total conductance due to one mol of solute remains unchanged. This, of course, is only the case with completely ionized solutes.

Determination of Electrical Conductance. The determination of the electrical conductance of a solution resolves itself into the determination of its resistance by a simple modification of the familiar Wheatstone-bridge method. The arrangement of the apparatus for this method devised by Kohlrausch * is represented diagrammatically in Fig. 89, where *ab* is the bridge wire, *B* is a resistance box, and *C* is a cell containing the solution whose resistance is to be measured. The points *d* and *c* are connected to a small induction coil *I* which gives an alternating current. This is necessary in order to prevent polarization which would occur if a direct current were used. The use of the alternating current necessitates the substitution of a telephone, *T*, for the galvanometer usually employed in measuring resistance. The positions of the induction coil and telephone are sometimes interchanged, but the arrangement shown in the diagram is to be preferred, since it insures a high electromotive force where the sliding

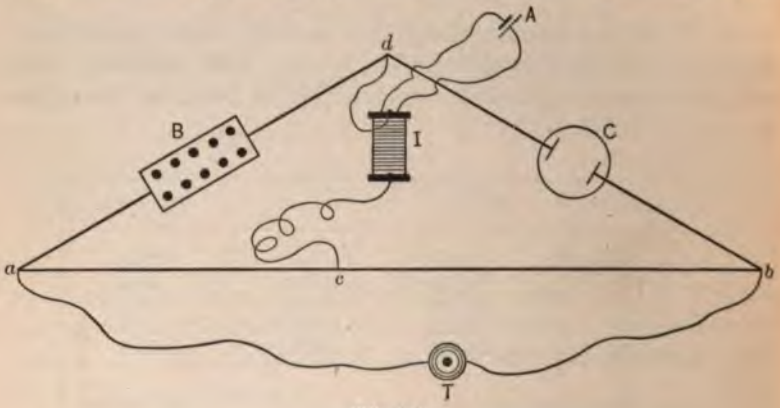


Fig. 89.

---

* Wied. Ann., 6, 145 (1879); 11, 653 (1880); 26, 161 (1885).

contact c touches the wire, this being the most uncertain connection in the entire arrangement. A small accumulator A, serves to operate the induction coil. In making a measurement, the coil is connected with the accumulator and the vibrator adjusted so that a high mosquito-like tone is emitted; then the sliding contact c is moved along the wire ab until the sound in the telephone reaches a minimum, the position of the point of contact with the bridge-wire being read on the millimeter scale placed below. According to the principle of the Wheatstone bridge, it follows that

$$\frac{C}{B} = \frac{bc}{ac}.$$

Since the resistance B and the lengths bc and ac are known, the resistance C can be calculated. Various types of conductance cells are in use, depending upon whether the solution has a high or a low resistance. The form shown in Fig. 90 is widely used. The two electrodes are made of platinum foil, connection with the mercury in the two glass tubes tt being established by means of two pieces of stout platinum wire sealed through the ends of these tubes. The tubes tt are fastened into a tight-fitting vulcanite cover so that the electrodes may be removed, rinsed and dried without altering their relative positions. Before the cell is used, the electrodes must be coated electrolytically with platinum black. It is not necessary to know the area of the electrodes or the distance between them, since it is possible to determine a factor, termed the *resistance capacity*, by means of which the results obtained with the cell can be transformed into reciprocal ohms. To this end the specific conductances of a number of standard solutions have been carefully determined by Kohlrausch; thus, for

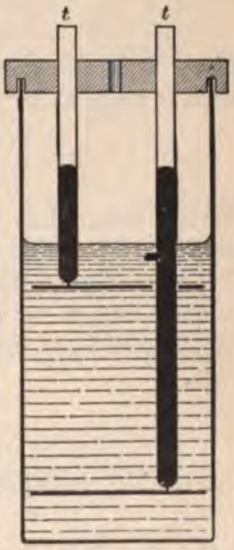


Fig. 90.

a 0.02 molar solution of potassium chloride he found the following values: —

$$\kappa_{18^\circ} = 0.002397 \quad \text{and} \quad \kappa_{25^\circ} = 0.002768,$$

or

$$\Lambda_{18^\circ} = 119.85 \quad \text{and} \quad \Lambda_{25^\circ} = 138.4.$$

Let the resistance of the cell when filled with 0.02 molar potassium chloride be C, then according to the principle of the Wheatstone bridge we have

$$C = B \cdot \frac{bc}{ac},$$

or denoting the conductance of the solution by L, we obtain

$$L = \frac{1}{C} = \frac{ac}{B \cdot bc}.$$

Since the specific conductance κ must be proportional to the observed conductance, we have

$$\kappa = KL = K\frac{ac}{B \cdot bc},$$

where K is the resistance capacity of the cell. If the measurement is made at 18° C., then we have

$$K = \frac{0.002397\, B \cdot bc}{ac}.$$

Having determined the resistance capacity of the cell we may then proceed to determine the conductance of any solution. For example, suppose that when the resistance in the box is B', the point of balance on the bridge-wire is at c', then the specific conductance of the solution will be

$$\kappa' = K\frac{ac'}{B'bc'}.$$

If κ' is multiplied by the volume of the solution, we obtain the equivalent conductance, or

$$\Lambda = \kappa' V.$$

Relative Conductances of Different Substances. The study of the electrical conductance of various solutes in aqueous solution, reveals the fact that electrolytes differ greatly in their conducting power. They may be roughly divided into two classes: —

ıe with high conducting power, such as strong acids, strong ɜs, and salts; and those with low conducting power, such as nonia and most of the organic acids and bases. Further-'e, the equivalent or molar conductance increases with the dilu-ı until a dilution of about 10,000 liters is reached, beyond ch it remains constant. The following table gives the equiv-ıt conductances of three typical electrolytes, V representing volume of the solution in liters, and Λ the equivalent con-:tance: —

HYDROCHLORIC ACID.

V	Λ (18°).
0.333	201.0
1.0	278.0
10.0	324.4
100.0	341.6
1000.0	345.5

SODIUM HYDROXIDE.

V	Λ (18°).
0.333	100.7
1.0	149.0
10.0	170.0
100.0	187.0
500.0	186.0

POTASSIUM CHLORIDE.

V	Λ (18°).
0.333	82.7
1.0	91.9
10.0	104.7
100.0	114.7
1,000.0	119.3
10,000.0	120.9

The curves shown in Fig. 91 are plotted from the data of the foregoing table, and bring out very clearly the differences in conducting power possessed by the three electrolytes.

In general the conductance of pure liquids is small. Thus, the specific conductance of pure water at 18° is approximately 1×10^{-6} reciprocal ohms and, as Walden * has shown, the specific conductance of a number of other solvents is of the same order as that for water. Mixtures of two liquids, each of which is practically non-conducting, may have a conductance differing but little from that of the two components; or the mixture may have a very high conductance. For example, the conductance of a mixture

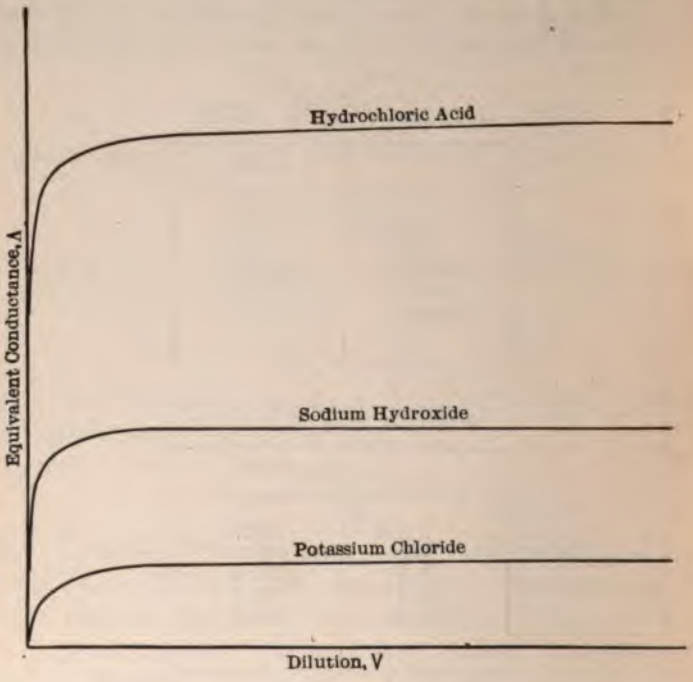


Fig. 91.

---

* Zeit. phys. Chem., 46, 103 (1903).

of water and ethyl alcohol is of the same order of magnitude as that of the two components, while on the other hand, a mixture of water and sulphuric acid, each of which in the pure state is practically a non-conductor, has great conducting power. The variation of the specific conductance of mixtures of water and sulphuric acid is represented in Fig. 92, the concentrations of sulphuric acid being plotted on the axis of abscissæ and the specific conductances on the axis of ordinates. It appears that as the concentration of the sulphuric acid increases, the specific conductance of the mixture increases until 30 per cent of acid is present, beyond which point it gradually diminishes. When pure sulphuric acid is present the value of the specific conductance is practically zero. On dissolving sulphur trioxide in the pure acid, the specific conductance increases slightly to a maximum and then falls rapidly to zero. There is a minimum in the curve corresponding to about 85 per cent of acid, a concentration which

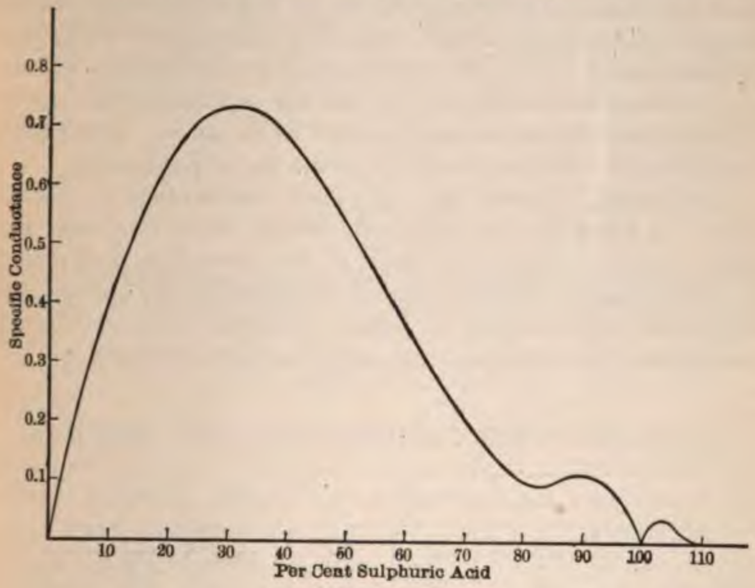


Fig. 92.

corresponds almost exactly with the hydrate $H_2SO_4.H_2O$. Why some liquid mixtures should have marked conducting power and others hardly any, it is difficult to explain. Many fused salts, such as silver nitrate and lithium chloride, are excellent conductors and are thus exceptions to the general rule, that pure substances belonging to the second class of conductors possess little conducting power.

The Law of Kohlrausch. The electrical conductance of solutions was systematically investigated by Kohlrausch who showed that the limiting value of the equivalent conductance, which may be represented by Λ_∞, is different for different electrolytes and may be considered as the sum of two independent factors, one of which refers to the cation and the other to the anion. This experimental result is commonly known as the law of Kohlrausch.

The limiting value of the equivalent conductance is reached when the molecules are completely broken down into ions, and under these conditions the whole of the electrolyte participates in conducting the current. The accompanying table, giving the equivalent conductances at infinite dilution of several binary electrolytes, illustrates the truth of the law of Kohlrausch.

EQUIVALENT CONDUCTANCES AT INFINITE DILUTION.

	K	Na	Li	NH_4	H	Ag
Cl	123	103	95	122	353	.....
NO_3	118	98	.....	.....	350	109
OH	228	201	.....	.....	.....	.....
ClO_3	115	.....	.....	.....	.....	103
$C_2H_3O_2$	94	73	.....	.....	.....	83

The differences between two corresponding sets of numbers in the same vertical column, and of any two corresponding sets of numbers in the same horizontal row will be found to be nearly equal. This could only occur when the limiting conductance is the sum of two entirely independent quantities. Each ion invariably carries the same charge of electricity and moves with its own velocity quite independent of the nature of its companion ion. Therefore, at infinite dilution, we have

$$\Lambda_\infty = l_c + l_a,$$

in which l_c and l_a are the equivalent conductances of the ions of the electrolyte at infinite dilution. From this it follows that

$$n = \frac{l_c}{l_c + l_a} = \frac{l_c}{\Lambda_\infty},$$

and

$$1 - n = \frac{l_a}{l_c + l_a} = \frac{l_a}{\Lambda_\infty};$$

or

$$l_c = n\Lambda_\infty,$$

and

$$l_a = (1 - n)\Lambda_\infty.$$

Thus, the equivalent conductance of silver nitrate at infinite dilution at 18° is 115.5, while $n = 0.518$ and $1 - n = 0.482$; therefore

$$l_c = 0.518 \times 115.5 = 60.8,$$

and

$$l_c = 0.482 \times 115.5 = 55.7;$$

or one gram-equivalent of silver ions possesses a conductance of 60.8 when placed between electrodes one centimeter apart and large enough to contain between them the entire volume of solution in which the $Ag^{\cdot}$ ions exist; and one gram-equivalent of NO_3' ions under the same conditions have a conductance equal to 55.7.

The values of the ionic conductances at infinite dilution remain constant in all solutions in the same solvent at the same temperature, so that it is possible to calculate the equivalent conductance for any substance at infinite dilution.

In the subjoined table are given the ionic conductances of various ions at 18° and infinite dilution, together with their temperature coefficients.

IONIC CONDUCTANCES AT INFINITE DILUTION.

Ion.	l_c	Temp. Coeff.
$Li^{\cdot}$	33.44	0.0265
$Na^{\cdot}$	43.55	0.0244
$K^{\cdot}$	64.67	0.0217
$Rb^{\cdot}$	67.6	0.0214
$Cs^{\cdot}$	68.2	0.0212
$NH_4^{\cdot}$	64.4	0.0222
$Tl^{\cdot}$	66.0	0.0215
$Ag^{\cdot}$	54.02	0.0229
F'	46.64	0.0238
Cl'	65.44	0.0216
Br'	67.63	0.0215
I'	66.40	0.0213
SCN'	56.63	0.0211
ClO_3'	55.03	0.0215
IO_3'	33.87	0.0234
NO_3'	61.78	0.0205
$H^{\cdot}$	318.0	....
OH'	174.0	....
$\frac{1}{2}\,Zn^{\cdot\cdot}$	45.6	0.0251
$\frac{1}{2}\,Mg^{\cdot\cdot}$	46.0	0.0256
$\frac{1}{2}\,Ba^{\cdot\cdot}$	56.3	0.0238
$\frac{1}{2}\,Pb^{\cdot\cdot}$	61.5	0.0243
$\frac{1}{2}\,SO_4''$	68.7	0.0227
$\frac{1}{2}\,CO_3''$	70.0	0.0270

In the case of weak electrolytes the value of Λ_∞ cannot be determined directly from conductance measurements, since before the limiting value is reached, the solution has become so dilute as to render accurate measurements of the specific conductance impossible. The law of Kohlrausch enables us to get around this difficulty. Thus, the value of Λ_∞ for acetic acid must be equal to the sum of the conductances of the $H^{\cdot}$ and CH_3COO' ions. The conductance of the $H^{\cdot}$ ion at 18° is, according to the preceding table, 318. The value of the conductance of the CH_3COO' ion can be determined from the conductance of sodium acetate at infinite dilution, Λ_∞ for this salt being 78.1 at 18°. Since the ionic conductance of the $Na^{\cdot}$ ion is 43.55 at 18°, it follows that the conductance of the CH_3COO' ion must be $78.1 - 43.55 = 34.55$. Therefore, for acetic acid we have

$$\Lambda_\infty = l_c + l_a = 318 + 34.55 = 352.55 \text{ at } 18°.$$

Bredig * has shown that the ionic conductance of elementary ions is a periodic function of the atomic weight. When the ionic conductances are plotted as ordinates against the atomic weights as abscissæ, the curve shown in Fig. 93 is obtained. A glance at the curve shows the periodic nature of the relation.

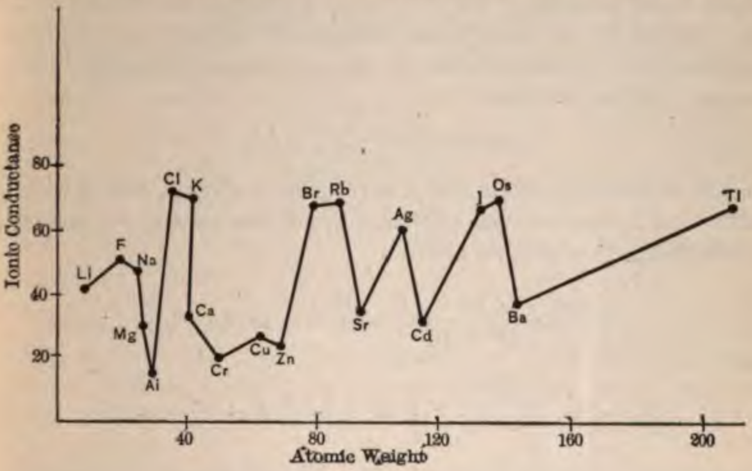


Fig. 93.

Absolute Velocity of the Ions. Thus far we have considered only the relative velocities of the ions and their conductances; we now proceed to the consideration of their absolute velocities in centimeters per second.

Let a current of electricity pass through a centimeter cube of a solution of a binary electrolyte. If the solution contains m mols of solute per liter, then $m/1000$ will be the number of mols in the centimeter cube. The charge on either the cation or the anion is $F\frac{m}{1000}$, where $F = 96{,}540$ coulombs. If C represents the total current, we have

$$C = F\frac{m}{1000}(l_c + l_a),$$

---

* Zeit. phys. Chem., 13, 242 (1894).

since the current is the charge which passes through one face of the cube in one second. In a centimeter cube, the current is equal to the product of the specific conductance and the difference of potential E, the latter being numerically equal to the potential gradient, the distance between the electrodes being one centimeter. Hence, we have

$$1000\,\kappa E = Fm\,(l_c + l_a).$$

If E is expressed in volts and κ in reciprocal ohms, l_c and l_a will be expressed in centimeters per second, for on passing to absolute electromagnetic units, we have

$$\frac{1000\,(\kappa \times 10^{-9})\,(E \times 10^{8})}{(F \times 10^{-1})} = m\,(l_c + l_a),$$

or

$$\frac{1000}{m}\kappa = F\,(l_c + l_a) = \Lambda_\infty,$$

where l_c and l_a are the ionic velocities for unit potential gradient – 1 volt per centimeter.

From this it follows that

$$\frac{\Lambda_\infty}{F} = u + v.$$

The equivalent conductance of a 0.0001 molar solution of potassium chloride at 18° is 128.9; the total velocity of the two ions is then,

$$\frac{128.9}{96{,}540} = 0.001345 \text{ cm. per sec.}$$

This total velocity is made up of the two individual ionic velocities. The transport numbers of the two ions, $K^{\cdot}$ and Cl', are respectively 0.493 and 0.507. Hence the absolute velocities of the ions, expressed in centimeters per second, in a 0.0001 molar solution of potassium chloride at 18° are as follows: —

$$u = 0.001345 \times 0.493 = 0.00066 \text{ cm. per sec.},$$

and

$$v = 0.001345 \times 0.507 = 0.00068 \text{ cm. per sec.}$$

The absolute velocities of some of the more common ions at 18° are given in the following table: —

ABSOLUTE IONIC VELOCITIES.

Ion.	Velocity.	Ion.	Velocity.
	cm. per sec.		cm. per sec.
$K^{\cdot}$	0.00066	$H^{\cdot}$	0.00320
$NH_4^{\cdot}$	0.00066	Cl'	0.00069
$Na^{\cdot}$	0.00045	NO_3'	0.00064
$Li^{\cdot}$	0.00036	ClO_3'	0.00057
$Ag^{\cdot}$	0.00057	OH'	0.00181
Cr_2O_7''	0.000473	$Cu^{\cdot\cdot}$	0.00031

The velocities of certain ions have been determined directly. Thus, the velocity of the hydrogen ion was measured by Lodge[*] in the following manner: — The tube *B*, Fig. **94**, 40 cm. long and 8 cm. in diameter, was graduated and bent at right angles at the ends. This was filled with an aqueous solution of sodium chloride in gelatine, colored red by the addition of an alkaline solution of phenolphthalein. When the contents of the tube had gelatinized, the latter was placed horizontally, connecting two beakers filled with dilute sulphuric acid as shown in the diagram. A current of electricity was passed from one electrode *A* to the other electrode *C*.

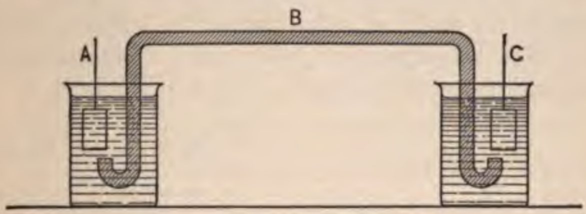


Fig. 94.

The hydrogen ions from the anode vessel were thus carried along the tube, and discharged the red color of the phenolphthalein as they migrated toward the cathode. In this manner the velocity of the hydrogen could be observed under a known potential gradient. The observed and calculated values agree excellently. It was shown that the velocity of the hydrogen ions suffered almost no retardation from the high viscosity of the gelatine solution. Whetham,* in his experiments on ionic velocity, employed two solutions one of which possessed a colored ion, the progress of the latter being observed and its velocity determined under unit potential gradient. For example, consider the boundary line between two equally dense solutions of the electrolytes AC and BC, C being a colorless and A a colored ion. When a current passes through the boundary between the two electrolytes, the anion C will migrate toward the positive electrode while the two cations, A and B, will migrate toward the negative electrode and the color boundary will move with the current, its speed being equal to that of the colored ion A. In this way Whetham measured the absolute velocities of the ions, $Cu^{\cdot\cdot}$, Cr_2O_7'', and Cl'. Ionic velocities have also been determined by Steele † who observed the change in the index of refraction of the solution as the ions migrated. The accompanying table gives a comparison of the calculated and observed velocities of some of the ions.

---

[*] Brit. Assoc. Report, p. 393 (1886).

Ion.	Velocity (obs.).	Velocity (calc.).
	cm. per sec.	cm. per sec.
$H^{\cdot}$	0.0026	0.0032
$Cu^{\cdot\cdot}$	0.00029	0.00031
Cl'	0.00058	0.00069
Cr_2O_7''	0.00047	0.000473

Conductance and Ionization. We have already seen that solutions of strong acids, strong bases and salts exert abnormally-great osmotic pressures. According to the molecular theory, this abnormal osmotic activity has been ascribed to the presence in the solutions of a greater number of dissolved particles than would be anticipated from the simple molecular formulas of the solutes. The ratio of the observed to the theoretical osmotic pressure was represented, according to van't Hoff, by the factor "i."

---

* Phil. Trans. A., **184**, 337 (1893); **196**, 507 (1895).

† Phil. Trans. A., **198**, 105 (1902).

In 1887, Arrhenius showed that there is an intimate connection between electrical conductance and abnormal osmotic activity, only those solutions conducting the electric current which exert abnormally-high osmotic pressures. It had already been pointed out by Kohlrausch, that the equivalent conductance of a solution increases at first with the dilution and then ultimately becomes constant. Arrhenius explained this behavior by assuming that the molecules of the solute are dissociated into ions, the conductance of the solution being solely dependent upon the number of ions present. The dissociation increases with the dilution until finally, when the equivalent conductance has reached its maximum value, it is complete, the molecules of solute being entirely broken down into ions. This theory of Arrhenius, known as the theory of electrolytic dissociation, is based, as has been pointed out, upon the views advanced by Clausius. Arrhenius showed how the degree of dissociation of an electrolyte can be calculated from the electrical conductance of its solutions. According to the theory of electrolytic dissociation, the conductance of a solution is dependent upon the number of ions present in the solution, upon their charges, and upon their velocities. Since the electric charges carried by equivalent amounts of the ions of different electrolytes are equal, and since the velocities of the ions for the same electrolyte are practically independent of the dilution of the solution, it follows that the increase in equivalent conductance with dilution must depend almost wholly upon the increase in the number of ions present.

The equivalent conductance at infinite dilution has been shown by the law of Kohlrausch to be

$$\Lambda_\infty = l_c + l_a,$$

and, therefore, the equivalent conductance at any dilution v, must be

$$\Lambda_v = \alpha\,(l_c + l_a),$$

where α is the degree of dissociation of the electrolyte. Dividing the second equation by the first, we obtain

$$\alpha = \frac{\Lambda_v}{\Lambda_\infty}.$$

This equation enables us to calculate the degree of ionization of an electrolyte at any dilution, provided the conductance of the solution at the particular dilution is known, together with its conductance, at infinite dilution. For example, Λ_v at 18° for a molar solution of sodium chloride is 74.3, and Λ_∞ is 110.3; therefore, $\alpha = 74.3 \div 110.3 = 0.673$, or in a molar solution, the molecules of sodium chloride are dissociated to the extent of 67.3 per cent. A comparison of the values of i based upon conductance and osmotic data has already been given in the table on page 230. Since $\Lambda_v = \alpha\,(l_c + l_a)$, we may also write

$$\frac{\Lambda_v}{F} = \alpha\,(u + v) \cdot$$

The Dissociation of Water. Water behaves as a very weak binary electrolyte, dissociating according to the equation,

$$H_2O \rightleftarrows H^{\cdot} + OH'.$$

The specific conductance of water, purified with the utmost care, has been determined by Kohlrausch and Heydweiller.* Their results are given in the following table: —

Temperature, degrees.	Specific Conductance$\times 10^{-6}$.
0	0.014
18	0.040
25	0.055
34	0.084
50	0.170

The conductance of pure water at 0° is so small that one millimeter of it has a resistance equal to that of a copper wire of the same cross-section and 40,000,000 kilometers in length, or in other words, long enough to encircle the earth one thousand times. Knowing the specific conductance of water, its degree of dissociation can be easily calculated. The ionic conductances of the two ions of water at 18° are as follows: — $H^{\cdot} = 318$, and $OH' =$

---

* Zeit. phys. Chem., 14, 317 (1894).

174. Therefore, the maximum equivalent conductance of water should be

$$\Lambda_\infty = 318 + 174 = 492.$$

The equivalent conductance at 18°, of a liter of water between electrodes 1 cm. apart is, according to the data of Kohlrausch,

$$0.04 \times 10^{-6} \times 10^{3} = 0.04 \times 10^{-3};$$

therefore

$$\frac{0.04 \times 10^{-3}}{492} = 0.8 \times 10^{-7} = c, \text{ the concentration of the ions,}$$

$H^{\cdot}$ and OH', in mols per liter at 18°.

Conductance of Difficultly-Soluble Salts. In a saturated solution of a difficultly-soluble salt, the solution is so dilute that in general we may assume complete ionization, or $\Lambda_v = \Lambda_\infty$.

When this is the case, we have

$$\kappa_{\text{solution}} - \kappa_{H_2O} = \kappa,$$

and

$$\Lambda_v = \Lambda_\infty = 1000\,\kappa V.$$

Hence

$$V = \frac{\Lambda_\infty}{1000\,\kappa};$$

or if m denotes the concentration in gram-equivalents per liter, we have

$$m = \frac{1}{V} = \frac{1000\,\kappa}{\Lambda_\infty}.$$

Thus, Böttger found for a saturated solution of silver chloride at 20°, $\kappa' = 1.374 \times 10^{-6}$. Deducting the specific conductance of the water at this temperature, we have

$$\kappa = 1.374 \times 10^{-6} - 0.044 \times 10^{-6} = 1.33 \times 10^{-6}.$$

Since the value of Λ_∞, at 20°, for silver chloride, determined from the table of ionic conductances, is 125.5, we have .

$$m = \frac{1000 \times 1.33 \times 10^{-6}}{125.5} = 1.06 \times 10^{-5} \text{ gr.-equiv. AgCl per liter.}$$

Temperature Coefficient of Conductance. When the temperature of a solution of an electrolyte is raised, the equivalent conductance usually increases. The increase in conductance is due, not to an increase in the ionization, but to the greater velocity of the ions caused by the diminution of the viscosity of the solution. According to Kohlrausch, the relation between conductance and temperature may be approximately expressed by the following equation,

$$\Lambda_t = \Lambda_{18^\circ}\{1 + \beta (t - 18)\},$$

where β is the temperature coefficient, or change in conductance for 1° C. Solving the equation for β, we have

$$\beta = \frac{\Lambda_t - \Lambda_{18^\circ}}{\Lambda_{18^\circ}(t - 18)}.$$

The temperature coefficients of several of the more common electrolytes are given in the accompanying table.

TEMPERATURE COEFFICIENTS OF CONDUCTANCE.

Electrolyte.	Temperature Coefficient.
Nitric acid	0.0163
Sulphuric acid	0.0164
Hydrochloric acid	0.0165
Potassium hydroxide	0.0190
Potassium nitrate	0.0211
Potassium iodide	0.0212
Potassium bromide	0.0216
Potassium chlorate	0.0216
Silver nitrate	0.0216
Potassium chloride	0.0217
Ammonium chloride	0.0219
Potassium sulphate	0.0223
Copper sulphate	0.0225
Sodium chloride	0.0226
Sodium sulphate	0.0234
Zinc sulphate	0.0250

The temperature coefficient of conductance is not, however, a simple linear function of the temperature. The following empirical equations, expressing equivalent conductance at infinite dilution at any temperature *t* in terms of the conductance at 18°, have been derived by Kohlrausch: —

$$\Lambda_{\infty t} = \Lambda_{\infty 18^\circ}\{1 + \alpha(t - 18) + \beta(t - 18)^2\},$$

and

$$\beta = 0.0163(\alpha - 0.0174).$$

When the values of $\Lambda_{\infty 18^\circ}$, α, and β, as determined for a large number of electrolytes, are substituted in the above equation, he showed that $\Lambda_{\infty t}$ becomes equal to zero at a temperature approximating to − 40°. Kohlrausch suggested that each ion moving through the solution carries with it an "atmosphere" of solvent, and that the resistance offered to the motion of the ion is simply the frictional resistance between masses of pure water. This view is in harmony with the solvate theory discussed in an earlier chapter. Washburn * has calculated the degree of ionic hydration for several ions. He finds, for example, that the hydrogen ion carries with it 0.3 molecule of water, while the lithium ion is hydrated to the extent of 4.7 molecules of water.

Conductance at High Temperatures and Pressures. The conductance of several typical electrolytes, at temperatures ranging from that of the room up to 306°, have been measured by A. A. Noyes and his co-workers.† These determinations were made in a conductance cell especially constructed to withstand high pressures.

The results show that the values of Λ_∞ for binary electrolytes become more nearly equal with rise of temperature. This may be taken as an indication of the fact that the ionic velocities tend to become more nearly equal as the temperature rises. The conductance of ternary electrolytes increases uniformly with the temperature, and attains values which are considerably greater than those reached by binary electrolytes. This is what might be expected, since if an ion is bivalent, as in a ternary electrolyte, the driving force is greater, and the ion must move faster, and, consequently, the conductance must be greater.

---

* Jour. Am. Chem. Soc., 30, 322 (1909).

† Publication of Carnegie Institution, No. 63.

The temperature coefficient of conductance for binary electrolytes is greater between 100° and 156°, than below or above these temperatures. The temperature coefficients of ternary electrolytes increases uniformly with rising temperature. In the case of acids and bases, the rate of increase in conductance steadily diminishes as the temperature rises. The ionization decreases regularly with rise in temperature, the temperature coefficient of ionization being small between 18° and 100°. The effect of pressure on conductance was studied by Fanjung.* He found that the conductance increases slightly with increasing pressure. This result he interprets as being due to increased ionic velocity rather than to an increase in the number of ions present in the solution.

Conductance of Non-aqueous Solutions. A large amount of interesting and important work has been done in recent years upon the electrical conductance of solutions in non-aqueous solvents.

It is impossible to give even a brief survey of the results of these investigations, and we must limit ourselves to the statement of the following general conclusions: —†

(1) The conditions in non-aqueous solutions are much more complex than in aqueous solutions.

(2) In general, the laws which have been found to apply to aqueous solutions also apply to non-aqueous solutions.

(3) Different solvents appear to have different dissociating powers.

(4) The dissociating power appears to run parallel with the dielectric constant of the solvent.

Many interesting phenomena present themselves in connection with the conductance of electrolytes in mixed solvents, but for an account of this work the student must consult the original papers of Jones and his students. ‡

---

* Zeit. phys. Chem., 14, 673 (1894).

† "Elektrochemie der nichtwässrigen Lösungen," by G. Carrara, Ahren's "Sammlung Chemischer und chemisch-technischer Vortraege," Vol. XII.

‡ Publication of the Carnegie Institution, No. 80.

Ionizing Power of Solvents. Thomson * and Nernst † pointed out that if the forces which hold the atoms in the molecule are of electrical origin, then those liquids which possess large dielectric constants should have correspondingly great ionizing power. This is a direct consequence of Coulomb's law of electrostatic attraction, which may be expressed by the equation,

$$f = \frac{q_1 q_2}{Kd^2},$$

in which q_1 and q_2 denote two electric charges, d the distance between them, f the force of attraction and K the dielectric constant. Obviously the larger K becomes, the smaller will be the value of f; i. e., the more likely the molecule will be to break down into ions. That the above relation is approximately true may be seen from the following table: —

DIELECTRIC CONSTANTS.

Solvent.	K	Ionizing Power.
Benzene	2.3	Extremely weak
Ethyl ether	4.1	Weak
Ethyl alcohol	25	Fairly strong
Formic acid	62	Strong
Water	80	Very strong
Hydrocyanic acid	96	Very strong

Dutoit and Aston ‡ have suggested that there is a connection between the ionizing power of a solvent and its degree of association, and Dutoit and Friderich § conclude that the values of Λ_∞, for a given electrolyte dissolved in different solvents, are a direct function of the degree of association and an inverse function of the viscosity of the solvents. Water and the alcohols furnish good illustrations of the truth of this generalization.

---

* Phil. Mag., **36**, 320 (1893).
† Zeit. phys. Chem., **13**, 531 (1894).
‡ Compt. rend., **125**, 240 (1897).
§ Bull. Soc. Chim. [3], **19**, 321 (1898).

Conductance of Fused Salts. While solid salts are exceedingly poor conductors of electricity, yet as the temperature is raised their conductance increases until at their melting point they may be grouped with good conductors. There is no sudden increase in conductance at the melting point. The specific conductance of a fused salt may exceed the specific conductance of the most concentrated aqueous solutions, but owing to the high concentration the equivalent conductance is much less. The following table gives the specific and equivalent conductance of fused silver nitrate: —

Temperature, degrees.	Sp. Cond.	Equiv. Cond.
218 (melt. pt.)	0.681	29.2
250	0.834	36.1
300	1.049	46.2
350	1.245	55.4

The specific conductance of a 60 per cent aqueous solution of silver nitrate at 18° is 0.208 reciprocal ohms.

If the salts are impure the conductance is raised, the effect of impurities being apparent even before the salts have reached their melting points. This is analogous to the behavior of solutions, and suggests that the impurity functions in the salt mixture as a dissolved solute.*

PROBLEMS.

1. An aqueous solution of copper sulphate is electrolyzed between copper electrodes until 0.2294 gram of copper is deposited. Before electrolysis the solution at the anode contained 1.1950 grams of copper, after electrolysis 1.3600 grams. Calculate the transport numbers of the two ions, $Cu^{\cdot\cdot}$ and SO_4''. *Ans.* $n = 0.28$, $1 - n = 0.72$.

2. A solution containing 0.1605 per cent of NaOH was electrolyzed between platinum electrodes. After electrolysis 55.25 grams of the cathode solution contained 0.09473 gram of NaOH, whilst the concentration of the middle portion of the electrolyte was unchanged. In a

---

* For a complete treatment of fused electrolytes the student is advised to consult, "Die Elektrolyse geschmolzener Salze," by Richard Lorenz.

silver coulometer the equivalent of 0.0290 gram of NaOH was deposited during electrolysis. Calculate the transport numbers of the $Na^{\cdot}$ and OH' ions. *Ans.* $n = 0.791$, $1 - n = 0.209$.

3. In a 0.01 molar solution of potassium nitrate, the transport numbers of the cation and anion are, respectively, 0.503 and 0.497. Find the equivalent conductances of the two ions in this solution having given that its specific conductance is 0.001044. *Ans.* $l_c = 52.5$, $l_a = 51.9$.

4. The absolute velocity of the $Ag^{\cdot}$ ion is 0.00057 cm. per sec., and that of the Cl' ion is 0.00059 cm. per sec. Calculate the equivalent conductance of an infinitely dilute solution of silver chloride.

5. The equivalent conductance of an infinitely dilute solution of ammonium chloride is 130; the ionic conductances of the ions OH' and Cl' are 174 and 65.44 respectively. Calculate the equivalent conductance of ammonium hydroxide at infinite dilution. *Ans.* $\Lambda_\infty = 238.56$.

6. The equivalent conductance of a molar solution of sodium nitrate at 18° is 66; its conductance at infinite dilution is 105.3. What is the degree of ionization in the molar solution? *Ans.* $\alpha = 62.6$ per cent.

7. The specific conductance of a saturated solution of AgCN at 20° is 1.79×10^{-6} and the specific conductance of water at the same temperature is 0.044×10^{-6} reciprocal ohms. The equivalent conductance at infinite dilution is 115.5. Calculate the solubility of AgCN in grams per liter. *Ans.* 2.02×10^{-3} gram/liter.

8. The equivalent conductance at 18° of a solution of sodium sulphate containing 0.1 gram-equivalent of salt per liter is 78.4, the conductance at infinite dilution is 113 reciprocal ohms. What is the value of i for the solution? What is its osmotic pressure?

Ans. $i = 2.388$; osmotic pressure = 2.85 atmos.

9. The freezing-point of a 0.1 molar solution of $CaCl_2$ is $-0°.482$. (a) Calculate the degree of ionization (freezing point constant = 1.89 for one mol per liter). (b) Calculate the degree of ionization from the equivalent conductance at 18°, which is 82.79 reciprocal ohms, whilst the equivalent conductance of $CaCl_2$ at infinite dilution is 115.8 reciprocal ohms. *Ans.* (a) $\alpha = 0.774$; (*b*) $\alpha = 0.715$.

CHAPTER XIX.

ELECTROLYTIC EQUILIBRIUM AND HYDROLYSIS.

Ostwald's Dilution Law. It has been shown in preceding chapters that the law of mass action is applicable to chemical equilibria in both gaseous and liquid systems. We now proceed to show that it applies equally to electrolytic equilibria. When acetic acid is dissolved in water it dissociates according to the equation

$$CH_3COOH \rightleftarrows CH_3COO' + H^{\cdot}.$$

Let one mol of acetic acid be dissolved in water and the solution diluted to v liters, and let α denote the degree of dissociation. Then, the concentration of the undissociated acid is $\frac{1-\alpha}{v}$, and the concentration of the ions is $\frac{\alpha}{v}$. Applying the law of mass action, we have

$$\left(\frac{\alpha}{v}\right)^2 = K\left(\frac{1-\alpha}{v}\right),$$

or

$$\frac{\alpha^2}{(1-\alpha)\,v} = K, \qquad (1)$$

where K is the *equilibrium or ionization constant.*

This equation expressing the relation between the degree of ionization and dilution, was derived by Ostwald[*] and is known as the Ostwald dilution law. Since $\alpha = \frac{\Lambda_v}{\Lambda_\infty}$, we may substitute this value of α in equation (1) and obtain the expression

$$\frac{\Lambda_v^2}{\Lambda_\infty\,(\Lambda_\infty - \Lambda_v)\,v} = K. \qquad (2)$$

---

[*] Zeit. phys. Chem., 2, 36 (1888); 3, 170 (1889).

The dilution law may be tested by substituting the value of α, corresponding to any dilution v, in the equation and calculating the value of the ionization constant, K; the value of α at any other dilution may then be calculated and compared with the value determined by direct experiment. The following table gives the results obtained with acetic acid at 14°.1, K being equal to 0.0000178:—

v (in liters).	$\alpha \times 10^2$ (calc.).	$\alpha \times 10^2$ (obs.).
0.994	0.42	0.40
2.02	0.60	0.614
15.9	1.67	1.66
18.1	1.78	1.78
1,500.0	15.0	14.7
3,010.0	20.2	20.5
7,480.0	30.5	30.1
15,000.0	40.1	40.8

As will be seen, the agreement between the observed and calculated values is very close. The table also shows to how small an extent the molecules of acetic acid are broken down into ions, a molar solution being dissociated less than 0.5 per cent. The dilution law holds for nearly all organic acids and bases, but fails to apply to salts, strong acids, and strong bases. When α is small, the term $(1 - \alpha)$ does not differ appreciably from unity, and equation (1) becomes

$$\frac{\alpha^2}{v} = K,$$

or

$$\alpha = \sqrt{vK}. \tag{3}$$

On the other hand, when α cannot be neglected, we have, on solving equation (2) for α,

$$\alpha = -\frac{vK}{2} + \sqrt{vK + \frac{v^2K^2}{4}}. \tag{4}$$

The method of derivation indicates that the dilution law is only strictly applicable to binary electrolytes and, therefore, it is improbable that it will hold for electrolytes yielding more than two ions. It has been found, however, that organic acids whether they are mono-, di-, or polybasic always ionize as a monobasic acid up to the dilution at which $\alpha = 50$ per cent. This means that the dilution law is applicable to polybasic acids up to that dilution at which the acid is 50 per cent ionized.

Strength of Acids and Bases. There are several methods by which the relative strengths of acids can be estimated. A method which has proved of great value is that in which two different acids are allowed to compete for a certain base, the amount of which is insufficient to saturate both of them. Suppose equivalent weights of nitric and dichloracetic acids together with sufficient potassium hydroxide to saturate one acid completely are taken: we then determine the position of the equilibrium represented by the equation

$$HNO_3 + CHCl_2 \cdot COOK \rightleftarrows CHCl_2 \cdot COOH + KNO_3.$$

In order to determine the conditions of equilibrium we may make use of any method which does not disturb this equilibrium. Since ordinary chemical methods are excluded on this account, we employ any physical property which is capable of exact measurement and differs sufficiently in the two systems, as for example, the change in volume, or the thermal change, accompanying neutralization. Thus, Ostwald * found that when one mol of potassium hydroxide is neutralized by nitric acid in dilute solution, the volume increases approximately 20 cc. When one mol of potassium hydroxide is neutralized by dichloracetic acid, however, the increase in volume is 13 cc. It is evident, therefore, that if nitric acid completely displaces dichloracetic acid as represented by the above equation, the increase in volume will be $20 - 13 = 7$ cc.; if no displacement occurs, then the volume will remain constant. He found that the volume actually increased 5.67 cc. Therefore, the reaction represented by the upper arrow has proceeded to the extent of $5.67 \div 7 = 80$ per cent. That is to say, in the competition of the two acids for the base, the nitric acid has taken 80 per cent and the dichloracetic acid has taken 20 per cent, or the relative strengths of the two acids are in the ratio of 80 : 20, or 4 : 1.

---

* Jour. prakt. Chem. [2], **18**, 328 (1878).

The relative strengths of acids can also be determined from their catalytic effect on the rates of certain reactions, such as the hydrolysis of esters or the inversion of cane sugar.

The order of the activity of acids is the same whether measured by equilibrium or kinetic methods. Arrhenius pointed out that the relative strengths of acids can be readily determined from their electrical conductance. The order of the strengths of acids as determined by equilibrium and kinetic methods is the same as that of their electrical conductances in equivalent solutions. This is well illustrated by the following table in which the three methods are compared, hydrochloric acid being taken as the standard of comparison: —

Acid.	Method Employed.		
	Equilibrium.	Kinetic.	Conductance.
HCl	100	100	100
HNO_3	100	100	99.6
H_2SO_4	49	53.6	65.1
$CH_2ClCOOH$	9	4.8	4.8
CH_3COOH	...	0.4	1.4

The results of these and other experiments warrant the conclusion that the strength of an acid is determined by the number of hydrogen ions which it yields. It is important to note that the electrical conductance of an acid is not directly proportional to its hydrogen ion concentration; the relatively high velocity of the H ion is the cause of the approximate proportionality between these two variables. In the case of a weak acid, the value of the ionization constant may be taken as a measure of the strength of the acid. The following table gives the values of the ionization constants at 25° for several different acids.

IONIZATION CONSTANTS OF ACIDS.

Acid.	Ionization Constant.
Acetic acid..................	0.0000180
Monochloracetic acid........	0.00155
Trichloracetic acid...........	1.21
Cyanacetic acid..............	0.0037
Formic acid.................	0.000214
Carbonic acid................	3040×10^{-10}
Hydrocyanic acid............	570×10^{-10}
Hydrogen sulphide...........	13×10^{-10}
Phenol......................	1.3×10^{-10}

Since for a weak acid, $\alpha = \sqrt{vK}$, it follows that for two weak acids at the same dilution, we may write

$$\frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_1}{K_2}},$$

or the ratio of the degrees of ionization of the two acids is equal to the square root of the ratio of their ionization constants. Thus, from the data given in the foregoing table for acetic and monochloracetic acids, we have

$$\frac{\alpha_1}{\alpha_2} = \sqrt{\frac{0.000018}{0.00155}} = \frac{1}{9.3},$$

or the effect of replacing one atom of hydrogen in the methyl group of acetic acid increases the strength of the acid about nine times.

Just as the hydrogen ion concentration of acids determines their strength, so the strength of bases is determined by the concentration of hydroxyl ions. The strength of bases may be estimated by methods similar to those employed in determining the strength of acids. Thus, two different bases may be allowed to compete for an amount of acid sufficient to saturate only one of them; or a catalytic method developed by Koelichen * may be used. This method is based upon the effect of hydroxyl ions on the rate of condensation of acetone to diacetonyl alcohol, as represented by the equation

$$2\,CH_3COCH_3 = CH_3COCH_2C\,(CH_3)_2OH.$$

---

* Zeit. phys. Chem., 33, 129 (1900).

In addition to these two methods, the method of electrical conductance is also applicable. The agreement between the results obtained by the three methods is quite satisfactory. The alkali and alkaline earth hydroxides are very strong bases and are dissociated to about the same extent as equivalent solutions of hydrochloric and nitric acids, while on the other hand, ammonia and many of the organic bases are very weak. The following table gives the ionization constants of several typical bases: —

IONIZATION CONSTANTS OF BASES.

Base.	Ionization Constant.
Ammonia	0.000023
Methylamine	0.00050
Trimethylamine	0.000074
Pyridine	2.5×10^{-10}
Aniline	1.1×10^{-10}

Mixtures of Two Electrolytes with a Common Ion. Just as the dissociation of a gaseous substance is diminished by the addition of an excess of one of the products of dissociation, so the ionization of weak acids and bases is depressed by the addition of a salt with an ion common to the acid or the base. If the degree of ionization of a salt with an ion in common with an acid or a base is represented by α', and n denotes the number of molecules of salt present, then the equation of equilibrium of the acid or base will be

$$(n\alpha' + \alpha)\,\alpha = Kv\,(1 - \alpha),$$

where α is the degree of ionization of the acid or base. For very weak acids and bases, α is so small that $1 - \alpha$ does not differ appreciably from unity, and since α' is practically independent of the dilution, we obtain

$$n\alpha = Kv$$

or

$$\alpha = \frac{Kv}{n}.$$

That is, the ionization of a weak acid or base, in the presence of one of its salts, is approximately inversely proportional to the amount of salt present.

In many of the processes of analytical chemistry, advantage is taken of the action of neutral salts on the ionization of weak acids and bases. Thus, while the concentration of hydroxyl ions in ammonium hydroxide is sufficient to precipitate magnesium hydroxide from solutions of magnesium salts, the presence of a small amount of ammonium chloride depresses the ionization of the ammonium hydroxide to such an extent that precipitation no longer takes place.

Isohydric Solutions. Arrhenius[*] was the first to point out what relation must exist between solutions of two electrolytes with a common ion, in order that, when mixed in any proportions, they may not exert any mutual influence. He showed that when the concentration of the common ion in each of the two solutions is the same before mixing, no alteration in the degree of ionization will occur after mixing. Such solutions are said to be *isohydric*. Thus, an aqueous solution containing one mol of acetic acid in 8 liters, is isohydric with an aqueous solution containing one mol of hydrochloric acid in 667 liters. On mixing these two solutions the hydrogen ion concentration remains unchanged, and if the mixture is treated with a small amount of sodium hydroxide, equal amounts of sodium acetate and sodium chloride will be formed.

That isohydric solutions may be mixed without altering their respective ionizations may be shown in the following manner: — Let C and c denote the concentrations of the undissociated portions, and C_A, C_2, c_A, and c_2 denote the concentrations of the dissociated portions of two electrolytes, and let C_2 and c_2 correspond to two different ions.

Then, we have

$$kc = c_A c_2, \tag{1}$$

and

$$KC = C_A C_2. \tag{2}$$

---

[*] Wied. Ann., 30, 51 (1887).

If v liters of the first solution be mixed with V liters of the second solution, the concentrations of the undissociated portions, and of the dissimilar ions, will be

$$\frac{Cv}{V+v}, \quad \frac{cv}{V+v}, \quad \frac{C_2V}{V+v}, \quad \text{and} \quad \frac{c_2v}{V+v},$$

while the concentration of the common ion A, becomes

$$\frac{C_AV + c_Av}{V+v}.$$

Applying the law of mass action, we have

$$kc = \frac{C_AV + c_Av}{V+v}c_2, \qquad (3)$$

and

$$KC = \frac{C_AV + c_Av}{V+v}C_2. \qquad (4)$$

But equations (3) and (4) only become identical with equations (1) and (2) when $C_A = c_A$, or in other words, no change in the degree of dissociation takes place after the two solutions are mixed.

Ionization of Strong Electrolytes. It has already been mentioned that the Ostwald dilution law, which is a direct consequence of the law of mass action, applies only to weak electrolytes. Just why the law of mass action should fail to apply to strong electrolytes is not known, but several possible causes have been suggested to account for its failure. One of the most plausible explanations is that advanced by Biltz,* who attributes the failure of the law of mass action when applied to strong electrolytes, to hydration of the solute. If the ions become associated with a large proportion of the solvent, the effective ionic concentration would then be the ratio of the amount of the ion present to that of the free solvent, instead of to the total solvent, as ordinarily calculated. This view is in harmony with certain facts which have been adduced in favor of the theory of solvation. While the Ostwald dilution law does not apply to strongly ionized electrolytes, certain empirical expressions have been derived which hold fairly well over a wide range of dilution. Thus, Rudolphi* showed that the equation

---

* Zeit. phys. Chem., 40, 218 (1902).

$$\frac{\alpha_2}{(1-\alpha)\sqrt{v}} = K',$$

gives approximately constant values for K' for strong electrolytes. The following table gives the results obtained with solutions of silver nitrate at 25°; the numbers in the third column being calculated by means of the Ostwald dilution law, while those in the fourth column are calculated by means of Rudolphi's dilution law.

v	α	K	K'
16	0.8283	0.253	1.11
32	0.8748	0.191	1.16
64	0.8993	0.127	1.06
128	0.9262	0.122	1.07
256	0.9467	0.124	1.08
512	0.9619	0.125	1.09

The Rudolphi equation was modified by van't Hoff † to the form

$$\frac{\alpha^3}{(1-\alpha)^2 v} = K''.$$

This equation holds even more closely than that of Rudolphi. Of the more recent empirical equations which have been derived to express the change of conductance of an electrolyte with dilution, the equations of Kraus * and Bates † deserve special mention.

The equation of Kraus has the following form: —

$$\left(\frac{\Lambda\eta}{\Lambda_0\eta_0}\right)^2 \frac{C}{\left(1-\frac{\Lambda\eta}{\Lambda_0\eta_0}\right)} = k + k'\left(\frac{C\Lambda\eta}{\Lambda_0\eta_0}\right)^h.$$

In this equation Λ is the conductance of the electrolyte whose concentration C is expressed in mols per liter, η/η_0 is the ratio of the viscosity of the solution to that of the solvent, and k, k', h, and Λ_0

---

* Jour. Am. Chem. Soc., **35**, 1412 (1913).

† Ibid., **37**, 1421 (1915).

re empirical constants the values of which are so chosen as to sure close agreement between the observed and calculated values f the conductance.

The equation of Bates is similar to that of the preceding equaion, except that the logarithm of the left-hand side of the equation substituted for the original expression of Kraus. The equation f Bates takes the form: —

$$\log_{10}\left(\frac{\Lambda\eta}{\Lambda_0\eta_0}\right)^2 \frac{C}{\left(1-\frac{\Lambda\eta}{\Lambda_0\eta_0}\right)} = k + k'\left(\frac{C\Lambda\eta}{\Lambda_0\eta_0}\right)^h.$$

he constants k, k', and h are purely empirical as in the equation f Kraus, but Λ_0 denotes the equivalent conductance at infinite ilution.

A comparison between the two equations is afforded by the folwing table in which is recorded the observed and calculated alues of the "corrected" equivalent conductance, $\Lambda\eta/\eta_0$, for lutions of potassium chloride at 18°.

COMPARISON OF THE EQUATIONS OF KRAUS AND BATES.

C	η/η_0	Λ (obs.)	$\Lambda\eta/\eta_0$	$\Lambda\eta/\eta_0$ (K.)	$\Lambda\eta/\eta_0$ (B.)
3	0.9954	88.3	87.89	87.4	89.3
2	0.9805	92.53	90.73	90.9	91.9
1	0.982	98.22	96.5	96.4	96.53
0.5	0.9898	102.36	101.32	101.1	101.29
0.2	0.9959	107.90	107.46	107.6	107.43
0.1	0.9982	111.97	111.77	111.9	111.73
0.05	0.9991	115.69	115.59	115.5	115.58
0.02	0.9996	119.90	119.85	119.8	119.83
0.01	0.9998	122.37	122.35	122.4	122.32
0.005	0.9999	124.34	124.33	124.4	124.38
0.002	1.0000	126.24	126.24	126.3	126.31
0.001	....	127.27	127.27	127.2	127.32
0.0005	....	128.04	128.04	127.6	128.05
0.0002	....	128.70	128.70	127.9	128.68
0.0001	....	129.00	129.00	128.1	128.96
0.0	....	129 50	129.50	128.3	129.50

It will be observed that for dilute solutions, the ratio η/η_0 is ractically unity and, furthermore, that the value of $C\Lambda/\Lambda_0$ is so nall that the second term on the right-hand side of both equations negligible in comparison with the value of k.

Therefore, under these conditions, both equations reduce to the form

$$\frac{\Lambda^2 C}{\Lambda_0 (\Lambda_0 - \Lambda)} = \text{constant},$$

which will be recognized as identical with Ostwald's dilution law as given on page 422.

Heat of Ionization. The heat of ionization of an electrolyte can be calculated by means of the reaction isochore equation of van't Hoff (see p. 324), provided the degree of ionization at two different temperatures is known.

Since

$$K_1 = \frac{\alpha_1^2}{(1 - \alpha_1) v},$$

and

$$K_2 = \frac{\alpha_2^2}{(1 - \alpha_2) v},$$

it follows that the heat of ionization may be calculated by means of the equation

$$Q = \frac{2.306\, R \left\{ \log \frac{\alpha_1^2}{(1 - \alpha_1) v} \log \frac{\alpha_2^2}{(1 - \alpha_2) v} \right\} T_1 T_2}{T_1 - T_2}.$$

Arrhenius * has shown that this equation also applies to those electrolytes which do not obey the Ostwald dilution law. Some of the results obtained by Arrhenius are given in the accompanying table: —

Electrolyte.	Temperature.	Calories.
Acetic acid	35°	386
	21°.5	−28
Propionic acid	35°	557
	21°.5	183
Butyric acid	35°	935
	21°.5	427
Phosphoric acid	35°	2458
	21°.5	2103
Hydrochloric acid	35°	1080
Potassium chloride	35°	362
Potassium bromide	35°	425
Potassium iodide	35°	916
Sodium chloride	35°	454
Sodium hydroxide	35°	1292
Sodium acetate	35°	391

---

* Zeit. phys. Chem., 4, 96 (1889).

It will be found that the values of the heats of ionization given in this table do not agree with the values calculated for these same substances from the data given in the table on page 307. The reason for this lack of agreement is, that the data of the earlier table refer to the heat of formation of the ions from the dissolved substance, whereas the data of the table just given represent the combined thermal effects of solution and ionization.

The Solubility Product. While the law of mass action does not in general apply to the equilibrium between the dissociated and undissociated portions of an electrolyte, — except in the case of organic acids and bases, — it does apply with a fair degree of accuracy to saturated solutions of electrolytes.

A saturated solution of silver chloride affords an example of such an equilibrium. This salt is practically completely ionized in a saturated solution, as represented by the equation

$$\mathrm{AgCl} \rightleftarrows \mathrm{Ag}^{\cdot} + \mathrm{Cl}'.$$

Applying the law of mass action to this equilibrium, we obtain

$$\frac{c_{\mathrm{Ag}^{\cdot}} \times c_{\mathrm{Cl}}}{c_{\mathrm{AgCl}}} = K.$$

Since the solution is saturated, the value of c_{AgCl} must remain constant at constant temperature, and therefore

$$c_{\mathrm{Ag}^{\cdot}} \times c_{\mathrm{Cl}'} = \text{constant} = s,$$

where the product of the ionic concentrations s is called the *solubility* or *ionic product*.

The equilibria in the above heterogeneous system may be represented thus: —

$$\mathrm{Ag}^{\cdot} + \mathrm{Cl}' \rightleftarrows \underset{\text{(in solution)}}{\mathrm{AgCl}} \rightleftarrows \underset{\text{(solid)}}{\mathrm{AgCl}}.$$

The solubility product for silver chloride at 25° is 1.56×10^{-10}, the ionic concentrations being expressed in mols per liter. Hence, since the two ions are present in equivalent amounts, a saturated solution of silver chloride at 25° must contain $\sqrt{1.56 \times 10^{-10}} = 1.25 \times 10^{-5}$ mols per liter of $\mathrm{Ag}^{\cdot}$ and Cl' ions. In general, if

$$nA \rightleftarrows n_1A_1 + n_2A_2$$

represents the equilibrium between an electrolyte and its products of dissociation in saturated solution, we have

$$c_{A_1}^{n_1} \cdot c_{A_2}^{n_2} = s.$$

The solubility product may be defined as the maximum product of the ionic concentrations of an electrolyte which can exist at any one temperature.

Just as the dissociation of a gaseous substance or of an organic acid is depressed by the addition of one of the products of dissociation, so when a substance with a common ion is added to the saturated solution of an electrolyte, the dissociation is depressed and the undissociated substance is precipitated.

The following example will serve to illustrate how the solubility product of a substance can be determined, and how the change in solubility due to the addition of a substance containing a common ion may be calculated. The solubility of silver bromate at 25° is 0.0081 mol per liter. If we assume complete ionization, the concentration of the ions, $Ag^{\cdot}$ and BrO_3' will be the same and equal to 0.0081 mol per liter, or

$$(0.0081)\ (0.0081) = s.$$

The solubility in a solution of silver nitrate containing **0.1** mol of $Ag^{\cdot}$ ions can be calculated from the equation

$$(0.0081)^2 = (0.0081 + 0.1 - x)\ (0.0081 - x),$$

where x represents the amount of silver bromate thrown out of solution by the addition of 0.1 mol of $Ag^{\cdot}$ ion. Since $(0.0081 - x)$ represents the concentration of $Ag^{\cdot}$ and BrO_3' ions after the addition of the silver nitrate, it also represents the solubility of silver bromate under similar conditions. The effect of adding a solution of a soluble bromate containing 0.1 mol of BrO_3' ion will be the same as that produced by 0.1 mol of $Ag^{\cdot}$ ion.

The Basicity of Organic Acids. The Ostwald dilution law holds strictly for all monobasic organic acids, and also for polybasic organic acids which are less than 50 per cent ionized. The neutral salts of these acids, however, are much more highly ionized, and the difference in conductance between two dilutions of a neutral salt of a polybasic acid is greater than the difference in conductance between the same dilutions of a neutral salt of a monobasic acid. Ostwald * has shown that it is possible to estimate the basicity of an organic acid from the difference in the equivalent conductance of its sodium salt at two different dilutions.

As the result of a long series of experiments, he found that the difference between the equivalent conductance of the sodium salt of a monobasic organic acid at $v = 32$ liters and at $v = 1024$ liters is approximately 10 units. Similarly, the difference for a dibasic acid between the same dilutions is 20 units, and for an n-basic acid the difference is $10\,n$. Hence, to estimate the basicity of an organic acid, the equivalent conductance of its sodium salt at $v = 32$ liters and at $v = 1024$ liters is determined; then, if Δ is the difference between the values of the conductance at the two dilutions, the basicity will be $n = \frac{\Delta}{10}$.

The following table gives the values of Δ and n for the sodium salts of several typical organic acids: —

Acid.	Δ	n
Formic	10.3	1
Acetic	9.5	1
Propionic	10.2	1
Benzoic	8.3	1
Quininic	19.8	2
Pyridine-tricarboxylic (1, 2, 3)	31.0	3
Pyridine-tricarboxylic (1, 2, 4)	29.4	3
Pyridine-tetracarboxylic	41.8	4
Pyridine-pentacarboxylic	50.1	5

Influence of Substitution on Ionization. Attention has already been called to the marked difference in the strength of acetic acid produced by the replacement of the hydrogen atoms of the methyl group by chlorine. In the accompanying table the ionization constants for various substitution products of acetic acid are given: —

---

* Zeit. phys. Chem., **1**, 105 (1887); **2**, 902 (1888).

Acid.	Ionization Constant (25°).
Acetic, CH_3COOH	0.000018
Propionic, CH_3CH_2COOH	0.000013
Chloracetic, $CH_2ClCOOH$	0.00155
Bromacetic, $CH_2BrCOOH$	0.00138
Cyanacetic, $CH_2CNCOOH$	0.00370
Glycollic, $CH_2OHCOOH$	0.000152
Phenylacetic, $C_6H_5CH_2COOH$	0.000056
Amidoacetic, CH_2NH_2COOH	3.4×10^{-10}

This table affords an interesting illustration of the influence of different substituents on the strength of acetic acid. Thus, the activity of the acid is increased by the replacement of alkyl hydrogen atoms by Cl, Br, CN, OH, or C_6H_5, while the substitution of the CH_3 or NH_2 groups diminishes its activity. If we assume that the substituents retain their ion-forming capacity on entering into the molecule of acetic acid, these differences in activity can be readily explained. Thus, Cl, Br, CN, and OH tend to form negative ions, and hence increase the negative character of the group into which they enter. On the other hand, basic groups, such as NH_2, diminish the tendency of the group into which they enter to yield negative ions.

The influence of an alkyl residue on the strength of an organic acid is conditioned by its distance from the carboxyl group. This is well illustrated by the ionization constants of propionic acid and some of its derivatives.

Acid.	Ionization Constant (25°).
Propionic acid, CH_3CH_2COOH	0.0000134
Lactic acid, $CH_3CHOHCOOH$	0.000138
β-oxypropionic acid, CH_2OHCH_2COOH	0.0000311

The effect of the OH group in the α-position is seen to be much more marked than when it occupies the β-position.

The position of a substituent in the benzene nucleus exerts a marked influence on the strength of the derivatives of benzoic acid. The ionization constants of benzoic acid and the three chlorbenzoic acids are given in the following table: —

Acid.	Ionization Constant (25°).
Benzoic acid, C_6H_5COOH	0.000073
o-Chlorbenzoic acid, $C_6H_4ClCOOH$	0.00132
m-Chlorbenzoic acid, $C_6H_4ClCOOH$	0.000155
p-Chlorbenzoic acid, $C_6H_4ClCOOH$	0.000093

When the halogen enters the ortho-position, the strength of the acid is greatly augmented, while in the meta- and para- positions the effect is much smaller, meta-chlorbenzoic acid being stronger than para-chlorbenzoic acid. It is a general rule that the influence of substituents is always greatest in the ortho-position, and least in the meta- and para- positions, the order in the two latter being uncertain.

Hydrolysis. When a salt formed by a weak acid and a strong base, such as sodium carbonate, is dissolved in water, the solution shows an alkaline reaction, while on the other hand, when a salt formed by a strong acid and a weak base, such as ferric chloride, is dissolved in water, the solution shows an acid reaction.

The process which takes place in the aqueous solution of a salt, causing it to react alkaline or acid, is termed *hydrolysis* or *hydrolytic dissociation*. If MA represents a salt, in which M is the basic and A is the acidic portion, then the hydrolytic equilibrium may be represented by the equation

$$MA + H_2O \rightleftarrows MOH + HA.$$

If the base formed is insoluble or undissociated and the acid is dissociated, the solution will react acid. If the acid formed is insoluble or undissociated and the base is dissociated, the solution will react alkaline. Finally, if both base and acid are insoluble or undissociated, the salt will be completely transformed into base and acid, and, as there will be no excess of either $H^{\cdot}$ or OH' ions, the solution will remain neutral.

It is evident, then, that hydrolysis is due to the removel of either one or both of the ions of water by the ions of the salt to form undissociated or insoluble substances. As fast as the ions of water are removed, the loss is made good by the dissociation of more water, until eventually a condition of equilibrium is established. The conditions governing hydrolytic equilibrium may be determined from a knowledge of the solubility or ionic constant of the substances involved. Thus, if the product of the concentrations of the ions $M^{\cdot}$ and OH' exceeds that which can exist in pure water, then some undissociated or insoluble substance will be formed. This will disturb the equilibrium of $H^{\cdot}$ and OH' ions, and a further dissociation of water must occur until the ionic product of water is just reached.

If now the ions $H^{\cdot}$ and A' do not unite to form undissociated acid, the presence of an excess of $H^{\cdot}$ ions will disturb the equilibrium between pure water and its products of dissociation; or, since

$$c_{H^{\cdot}} \times c_{OH'} = s_{H_2O},$$

the concentration of OH' ions present, when $c_{H^{\cdot}}$ represents the total concentration of $H^{\cdot}$ ions, will be $\frac{s_{H_2O}}{c_{H^{\cdot}}}$.

A similar readjustment will take place when an undissociated or insoluble acid and a dissociated base are formed.

We may now proceed to consider three different cases of hydrolysis, *viz.*, when the reaction is caused (1) by the base, (2) by the acid, and (3) by both base and acid.

CASE I. *The formation of an undissociated or insoluble base is primarily the cause of the hydrolysis, the acid formed being dissociated.*

Let the hydrolytic equilibrium be represented by the equation

$$MA + H_2O \rightleftarrows MOH + HA.$$

The reaction will proceed in the direction of the upper arrow until the product, $c_{M^{\cdot}} \times c_{OH'}$, exceeds that which can exist in the absence of an undissociated base. When equilibrium is established, we have

$$\text{final } c_{M^{\cdot}} \times \text{final } c_{OH'} = K_{MOH} \times c_{MOH} \text{ formed,} \qquad (1)$$

or if the base formed is practically insoluble, the equilibrium equation simplifies to the form

$$\text{final } c_{M^{\cdot}} \times \text{final } c_{OH'} = s_{MOH}, \qquad (2)$$

where s_{MOH} is the solubility product of the base. The condition of equilibrium represented by the equation

$$c_{\text{H}^\cdot} \times c_{\text{OH}'} = s_{\text{H}_2\text{O}}$$

must be fulfilled. It follows that the final concentration of the OH′ ions will be the quotient obtained by dividing the ionic product for water, at the temperature of the experiment, by the final concentration of the H˙ ion, this latter being wholly dependent upon the extent of the reaction and the degree of ionization of the acid formed. If the degree of hydrolysis of the salt be represented by x, and the degree of dissociation of the unhydrolyzed portion of the salt be denoted by α_s, then, if one mol of salt be dissolved in V liters of solution, the final concentration of M˙ ions will be $\frac{\alpha_s(1-x)}{V}$ and the final concentration of the undssiociated base will be $\frac{x}{V}$. The total acid formed will be $\frac{x}{V}$, and if α_a denotes the degree of dissociation of the acid, the concentration of the H˙ ions will be $\alpha_a\frac{x}{V}$. Substituting these values in equations (1) and (2), we obtain

$$\frac{\alpha_s(1-x)}{V}\cdot\frac{s_{\text{H}_2\text{O}}}{\alpha_a\frac{x}{V}} = K_{\text{MOH}} \times \frac{x}{V}, \tag{3}$$

and

$$\frac{\alpha_s(1-x)}{V}\cdot\frac{s_{\text{H}_2\text{O}}}{\alpha_a\frac{x}{V}} = s_{\text{MOH}}. \tag{4}$$

Simplifying equations (3) and (4), we have

$$\frac{x^2}{(1-x)V}\cdot\frac{\alpha_a}{\alpha_s} = \frac{s_{\text{H}_2\text{O}}}{K_{\text{MOH}}} = K_h, \tag{5}$$

and

$$\frac{x}{(1-x)}\cdot\frac{\alpha_a}{\alpha_s} = \frac{s_{\text{H}_2\text{O}}}{s_{\text{MOH}}} = K_h'. \tag{6}$$

From equations (5) and (6) it appears that the constant of hydrolysis can be found either from the ionic product for water and the ionization constant of the base, or from the ionic product for water and the solubility product of the base. Furthermore, if the base formed is insoluble, equation (6) shows that the degree of hydrolysis, x, is independent of the dilution of the salt, V.

CASE II. *The formation of an undissociated or insoluble acid is primarily the cause of the hydrolysis, the base formed being dissociated.* In this case hydrolysis takes place until the product $c_{H^{\cdot}} \times c_{A'}$ exceeds that which can exist in the absence of undissociated acid. When equilibrium is established, we have

$$\text{final } c_{H^{\cdot}} \times \text{final } c_{A'} = K_{HA} \times c_{HA} \text{ formed}, \tag{7}$$

or if the acid formed is practically insoluble, the equilibrium equation simplifies to the form

$$\text{final } c_{H^{\cdot}} \times \text{final } c_{A'} = s_{HA}. \tag{8}$$

Since the final $c_{H^{\cdot}} = s_{H_2O} \div$ final $c_{OH'}$, we have, final $c_{A'} = \dfrac{\alpha_s(1-x)}{V}$, final $c_{OH'} = \alpha_b \dfrac{x}{V}$, where α_h is the degree of dissociation of the base formed, and the final $c_{HA} = \dfrac{x}{V}$. Substituting these values in equations (7) and (8), we obtain

$$\frac{\alpha_s(1-x)}{V} \cdot \frac{s_{H_2O}}{\alpha_b \dfrac{x}{V}} = K_{HA} \times \frac{x}{V}, \tag{9}$$

and

$$\frac{\alpha_s(1-x)}{V} \cdot \frac{s_{H_2O}}{\alpha_b \dfrac{x}{V}} = s_{HA}. \tag{10}$$

Simplifying equations (9) and (10), we have

$$\frac{x^2}{(1-x)V} \cdot \frac{\alpha_b}{\alpha_s} = \frac{s_{H_2O}}{K_{HA}} = K_h, \tag{11}$$

and

$$\frac{x}{(1-x)} \cdot \frac{\alpha_b}{\alpha_s} = \frac{s_{H_2O}}{s_{HA}} = K_h'. \tag{12}$$

It is evident from equations (11) and (12), that the constant of hydrolysis can be found either from the ionic product for water and the ionization constant of the acid, or from the ionic product for water and the solubility product of the acid.

CASE III. *The formation of an acid and a base, both being slightly dissociated, is the cause of the hydrolysis.*

In this case let us assume that K_{HA} is smaller than K_{MOH}. Since the final $c_{OH'} = \frac{K_{MOH} \times c_{MOH}}{c_{M^{\bullet}}}$, and since both HA and MOH are slightly dissociated, we may write $c_{HA} = c_{MOH} = \frac{x}{V}$, and $c_{A'} = c_{M^{\bullet}} = \frac{\alpha_s(1-x)}{V}$.

Substituting these values in equation (7), we obtain

$$\frac{\alpha_s(1-x)}{V} \cdot \frac{s_{H_2O}}{\dfrac{K_{MOH}\,\frac{x}{V}}{\frac{\alpha_s(1-x)}{V}}} = K_{HA} \times \frac{x}{V}. \tag{13}$$

Simplifying equation (13), we obtain

$$\frac{x^2}{(1-x)} \cdot \frac{1}{\alpha^2} = \frac{s_{H_2O}}{K_{HA} \times K_{MOH}} = K_h. \tag{14}$$

From equation (14) we see that the constant of hydrolysis can be found from the ionic product for water and the ionization constants of the acid and the base. If both acid and base are practically insoluble, the reaction will be complete at all dilutions.

As an illustration of the application of the foregoing equations, we may take the calculation of the degree of hydrolytic dissociation of potassium cyanide in 0.1 molar solution at 25°. Potassium cyanide being a salt of a weak acid, the degree of hydrolysis can be calculated by means of the equation

$$\frac{x^2}{(1-x)\,V} \cdot \frac{\alpha_b}{\alpha_s} = \frac{s_{H_2O}}{K_{HA}} = K_h.$$

Since at 25°, $K_{HA} = 13 \times 10^{-10}$ and $s_{H_2O} = (0.91 \times 10^{-7})$, we have

$$K_h = \frac{s_{H_2O}}{K_{HA}} = \frac{(0.91 \times 10^{-7})}{13 \times 10^{-10}},$$

and since in dilute solution $a_1 = a_2 = 1$, we have

$$\frac{x^2}{(1 - x) \cdot 10} = \frac{0.91 \times 10^{-14}}{13 \times 10^{-10}},$$

or

$$x = 0.00836.$$

Experimental Determination of Hydrolysis. The degree of hydrolysis can be determined experimentally in several different ways. A very convenient method is that based upon measurements of electrical conductance. When a salt reacts hydrolytically with one mol of water, the limiting value of its equivalent conductance will be $\Lambda_A + \Lambda_B$, where Λ_A and Λ_B denote the equivalent conductances of the acid and base formed. If Λ is the equivalent conductance of the unhydrolyzed salt, and Λ_h is the actual conductance of the salt at the same dilution, then the increase in conductance corresponding to a degree of hydrolysis x will be $\Lambda_h - \Lambda$. The value of Λ may be found by determining the conductance of the salt in the presence of an excess of one of the products of hydrolysis and deducting from it the conductance of the substance added. Since if the hydrolysis were complete, the equivalent conductance would be $\Lambda_A + \Lambda_B - \Lambda$, we have

$$x = \frac{\Lambda_h - \Lambda}{\Lambda_A + \Lambda_B - \Lambda},$$

all conductances being measured at the same dilution and the same temperature. The following example will illustrate the use of this equation: — At 25°, the equivalent conductance of an aqueous solution of aniline hydrochloride is 118.6, the dilution being 99.2 liters. The equivalent conductance in the presence of an excess of aniline is 103.6, while the equivalent conductance of hydrochloric acid at the same dilution is 411. The conductance of pure aniline is so small as to be negligible. Substituting these values in the equation, we find

$$x = \frac{118.6 - 103.6}{411 - 103.6} = 0.0488.$$

Lundén * has shown how this method may be extended to cases where both acid and base are slightly dissociated.

---

* Jour. chim. phys., 5, 145, 574 (1907).

The Ionization Constant of Water. One of the most accurate methods known for the determination of the ionization constant of water is based upon measurements of the degree of hydrolytic dissociation of different salts. Thus Shields * found that a 0.1 molar solution of sodium acetate is 0.008 per cent hydrolyzed at 25°. We may consider the salt, as well as the sodium hydroxide formed from its hydrolysis, to be completely dissociated at this dilution. The ionization constant of the acetic acid formed is 0.000018 at 25°. Solving equation (11) (on page 440) for s_{H_2O}, and remembering that $\alpha_s = \alpha_b = 1$, we have

$$s_{H_2O} = K_{HA} \cdot \frac{x^{2}}{(1 - x)\,V}.$$

Substituting the above values in this expression, we obtain

$$s_{H_2O} = 0.000018 \cdot \frac{(0.00008)^2}{(1 - 0.00008) \times 10} = 1.16 \times 10^{-14},$$

and since the ions, $H^{\cdot}$ and OH', are present in equivalent amounts, we have

$$c_{H^{\cdot}} = c_{OH'} = \sqrt{1.16 \times 10^{-14}} = 1.1 \times 10^{-7} \text{ mol per liter.}$$

Kohlrausch obtained from his measurements of the conductance of pure water at 25°, $c_{H^{\cdot}} = c_{OH'} = 1.05 \times 10^{-7}$ mol per liter (see p. 415).

PROBLEMS.

1. At 25° the specific conductance of butyric acid at a dilution of 64 liters is 1.812×10^{-4} reciprocal ohms. The equivalent conductance at infinite dilution is 380 reciprocal ohms. What is the degree of ionization and the concentration of $H^{\cdot}$ ions in the solution? What is the ionization constant of the acid?

Ans. $\alpha = 0.0305$, $c_{H^{\cdot}} = 4.765 \times 10^{-4}$ mol per liter, $K = 1.5 \times 10^{-5}$.

2. The heat of neutralization of nitric acid by sodium hydroxide is 13,680 calories, and of dichloracetic acid, 14,830 calories. When one equivalent of sodium hydroxide is added to a dilute solution containing one equivalent of nitric acid and one equivalent of dichloracetic acid, 13,960 calories are liberated. What is the ratio of the strengths of the two acids? *Ans.* $HNO_3 : CHCl_2COOH :: 3.1 : 1$.

---

* Zeit. phys. Chem., **12**, 167 (1893).

3. For potassium acetate we have the following data: —

v	$\Lambda_{v(18°)}$
2	67.1
10	78.4
100	87.9
1000	91.9

and $l_{\infty \atop K^\bullet} = 64.67$, and $l_{\infty \atop CH_3COO'} = 35$. Compare the constants obtained by the Ostwald, Rudolphi, and van't Hoff dilution laws.

4. The ionization constant of a 0.05 molar solution of acetic acid is 0.0000175 at 18°, and 0.00001624 at 52°. Calculate the heat of ionization of the acid. To what temperature does this value correspond?

Ans. 416 calories at 35°.

5. At 20° the specific conductance of a saturated solution of silver bromide was 1.576×10^{-6} reciprocal ohms, and that of the water used was 1.519×10^{-6} reciprocal ohms. Assuming that silver bromide is completely ionized, calculate the solubility and the solubility product of silver bromide, having given that the equivalent conductances of potassium bromide, potassium nitrate, and silver nitrate at infinite dilution are 137.4, 131.3, and 121 reciprocal ohms respectively.

Ans. $c_{\text{AgBr}} = 4.49 \times 10^{-7}$ mol per liter, $s_{\text{AgBr}} = 2.02 \times 10^{-13}$.

6. The solubility of silver cyanate at 100° is 0.008 mol per liter. Calculate the solubility in solution of potassium cyanate containing 0.1 mol of $K^\bullet$ ions.

Ans. 6.4×10^{-4} mol per liter.

7. Calculate the degree of hydrolytic dissociation of a 0.1 molar solution of ammonium chloride, having given the following data: — $\alpha_s = 0.86$, $\alpha_a = 0.87$, $K_{\text{NH}_4\text{OH}} = 0.000023$, and $s_{\text{H}_2\text{O}} = (0.91 \times 10^{-7})^2$ at 25°.

Ans. $x = 0.006$ per cent.

8. In the reaction represented by the equation

$$MA_3 + 3\,H_2O = M\,(OH)_3 + 3\,HA,$$

the base formed is insoluble. Derive an expression for the constant of hydrolysis.

$$Ans.\ K_p = \frac{s^3_{\text{H}_2\text{O}}}{s_{\text{M(OH)}_3}} = \frac{(3\,x)^3}{(1 - x)v^2} \cdot \frac{\alpha_a{}^3}{\alpha_s}.$$

9. The equivalent conductance of aniline hydrochloride at a dilution of 197.6 liters is 126.7 reciprocal ohms, at 25°. The equivalent con-

ductance of aniline hydrochloride in the presence of an excess of aniline is 106.6; and the equivalent conductance of hydrochloric acid at the same dilution is 415. If the conductance of pure aniline is negligible, calculate the degree of hydrolytic dissociation and the constant of hydrolysis, assuming $\alpha_s = \alpha_a = 1$.

Ans. $x = 6.52$ per cent, $K_h = 2.30 \times 10^{-5}$.

10. The hydrolysis constant of aniline is 2.25×10^{-5}, and the ionization constant is 5.3×10^{-10}. Calculate the concentration of the $\mathrm{H}^{\bullet}$ and OH' ions in water. *Ans.* $c_{\mathrm{CH}^{\bullet}} = c_{\mathrm{OH}'} = 1.09 \times 10^{-7}$.

3. For potassium acetate we have the following data:—

v	$\Lambda_{v(18^\circ)}$
2	67.1
10	78.4
100	87.9
1000	91.9

and $l_{\infty_{K^\cdot}} = 64.67$, and $l_{\infty_{CH_3COO'}} = 35$. Compare the constants obtained by the Ostwald, Rudolphi, and van't Hoff dilution laws.

4. The ionization constant of a 0.05 molar solution of acetic acid is 0.0000175 at 18°, and 0.00001624 at 52°. Calculate the heat of ionization of the acid. To what temperature does this value correspond?

Ans. 416 calories at 35°.

5. At 20° the specific conductance of a saturated solution of silver bromide was 1.576×10^{-6} reciprocal ohms, and that of the water used was 1.519×10^{-6} reciprocal ohms. Assuming that silver bromide is completely ionized, calculate the solubility and the solubility product of silver bromide, having given that the equivalent conductances of potassium bromide, potassium nitrate, and silver nitrate at infinite dilution are 137.4, 131.3, and 121 reciprocal ohms respectively.

Ans. $c_{AgBr} = 4.49 \times 10^{-7}$ mol per liter, $s_{AgBr} = 2.02 \times 10^{-13}$.

6. The solubility of silver cyanate at 100° is 0.008 mol per liter. Calculate the solubility in solution of potassium cyanate containing 0.1 mol of $K^\cdot$ ions. *Ans.* 6.4×10^{-4} mol per liter.

7. Calculate the degree of hydrolytic dissociation of a 0.1 molar solution of ammonium chloride, having given the following data:— $\alpha_s = 0.86$, $\alpha_a = 0.87$, $K_{NH_4OH} = 0.000023$, and $s_{H_2O} = (0.91 \times 10^{-7})^2$ at 25°.

Ans. $x = 0.006$ per cent.

8. In the reaction represented by the equation

$$MA_3 + 3\,H_2O = M\,(OH)_3 + 3\,HA,$$

the base formed is insoluble. Derive an expression for the constant of hydrolysis.

$$Ans.\ K_p = \frac{s^3{}_{H_2O}}{s_{M(OH)_3}} = \frac{(3\,x)^3}{(1-x)v^2} \cdot \frac{\alpha_a{}^3}{\alpha_s}.$$

9. The equivalent conductance of aniline hydrochloride at a dilution of 197.6 liters is 126.7 reciprocal ohms, at 25°. The equivalent con-

ductance of aniline hydrochloride in the presence of an excess of aniline is 106.6; and the equivalent conductance of hydrochloric acid at the same dilution is 415. If the conductance of pure aniline is negligible, calculate the degree of hydrolytic dissociation and the constant of hydrolysis, assuming $\alpha_s = \alpha_a = 1$.

Ans. $x = 6.52$ per cent, $K_h = 2.30 \times 10^{-5}$.

10. The hydrolysis constant of aniline is 2.25×10^{-5}, and the ionization constant is 5.3×10^{-10}. Calculate the concentration of the H˙ and OH′ ions in water. *Ans.* $c_{\mathrm{H}^{\bullet}} = c_{\mathrm{OH}'} = 1.09 \times 10^{-7}$.

3. For potassium acetate we have the following data:—

v	$\Lambda_{v(18^\circ)}$
2	67.1
10	78.4
100	87.9
1000	91.9

and $\underset{K^{\cdot}}{l_\infty} = 64.67$, and $\underset{CH_3COO'}{l_\infty} = 35$. Compare the constants obtained by the Ostwald, Rudolphi, and van't Hoff dilution laws.

4. The ionization constant of a 0.05 molar solution of acetic acid is 0.0000175 at 18°, and 0.00001624 at 52°. Calculate the heat of ionization of the acid. To what temperature does this value correspond?

Ans. 416 calories at 35°.

5. At 20° the specific conductance of a saturated solution of silver bromide was 1.576×10^{-6} reciprocal ohms, and that of the water used was 1.519×10^{-6} reciprocal ohms. Assuming that silver bromide is completely ionized, calculate the solubility and the solubility product of silver bromide, having given that the equivalent conductances of potassium bromide, potassium nitrate, and silver nitrate at infinite dilution are 137.4, 131.3, and 121 reciprocal ohms respectively.

Ans. $c_{AgBr} = 4.49 \times 10^{-7}$ mol per liter, $s_{AgBr} = 2.02 \times 10^{-13}$.

6. The solubility of silver cyanate at 100° is 0.008 mol per liter. Calculate the solubility in solution of potassium cyanate containing 0.1 mol of $K^{\cdot}$ ions. *Ans.* 6.4×10^{-4} mol per liter.

7. Calculate the degree of hydrolytic dissociation of a 0.1 molar solution of ammonium chloride, having given the following data:— $\alpha_s = 0.86$, $\alpha_a = 0.87$, $K_{NH_4OH} = 0.000023$, and $s_{H_2O} = (0.91 \times 10^{-7})^2$ at 25°.

Ans. $x = 0.006$ per cent.

8. In the reaction represented by the equation

$$MA_3 + 3\,H_2O = M\,(OH)_3 + 3\,HA,$$

the base formed is insoluble. Derive an expression for the constant of hydrolysis.

$$Ans.\ K_p = \frac{s^3_{H_2O}}{s_{M(OH)_3}} = \frac{(3\,x)^3}{(1-x)v^2} \cdot \frac{{\alpha_a}^3}{\alpha_s}.$$

9. The equivalent conductance of aniline hydrochloride at a dilution of 197.6 liters is 126.7 reciprocal ohms, at 25°. The equivalent con-

ductance of aniline hydrochloride in the presence of an excess of aniline is 106.6; and the equivalent conductance of hydrochloric acid at the same dilution is 415. If the conductance of pure aniline is negligible, calculate the degree of hydrolytic dissociation and the constant of hydrolysis, assuming $\alpha_s = \alpha_a = 1$.

Ans. $x = 6.52$ per cent, $K_h = 2.30 \times 10^{-5}$.

10. The hydrolysis constant of aniline is 2.25×10^{-5}, and the ionization constant is 5.3×10^{-10}. Calculate the concentration of the $H^{\bullet}$ and OH' ions in water. *Ans.* $c_{H^{\bullet}} = c_{OH'} = 1.09 \times 10^{-7}$.

CHAPTER XX.

ELECTROMOTIVE FORCE.

Galvanic Cells. Since the year 1800, when Volta invented his electric pile, many different forms of galvanic cell have been introduced.

It is not our purpose to give a detailed account of these cells, but rather to give a brief outline of the theories which have been advanced in explanation of the electromotive force developed in such cells. When two metallic electrodes are immersed in a solution of an electrolyte, a current will flow through a wire connecting the electrodes, provided the two metals are dissimilar, or that a difference exists between the solutions surrounding the electrodes. An electric current can be obtained from a combination of two different metals in the same electrolyte, from two different metals in two different electrolytes, from the same metal in different electrolytes, or from the same metal in two different concentrations of the same electrolyte.

In order that the electromotive force of the combination shall remain constant, it is necessary that the chemical changes involved in the production of the current shall neither destroy the difference between the electrodes, nor deposit upon either of them a non-conducting substance. A galvanic combination which fulfils these conditions very satisfactorily is the Daniell cell. This cell consists of zinc and copper electrodes immersed in solutions of their salts, as represented by the scheme

$$\text{Zn} - \text{Sol. of } \text{ZnSO}_4 \,\|\, \text{Sol. of } \text{CuSO}_4 - \text{Cu},$$

in which the two vertical lines indicate a porous partition separating the two solutions. When the zinc and copper electrodes are connected by a wire, a current of positive electricity passes from the copper to the zinc along the wire. Zinc dissolves from the zinc electrode, an equivalent amount of copper being displaced from the solution and deposited simultaneously on the copper electrode. As long as only a moderate current flows through the cell, the original nature of the electrodes is not modified, the only change which occurs being the gradual dilution of the copper sulphate, owing to the separation of copper and its replacement by zinc. If the loss of copper sulphate is replaced, the electromotive force of the cell will remain constant. If, after the cell is assembled no current be allowed to flow, the copper sulphate will slowly diffuse into the solution of zinc sulphate, and metallic copper will ultimately be deposited on the zinc electrode. In this way miniature, local galvanic cells will be formed on the surface of the zinc, and the metal dissolves as though the main circuit were closed. Until this deposition takes place, the cell may be left on open circuit without danger of deterioration. Unless chemically pure zinc is used, local action is likely to occur, owing to the formation of local galvanic couples between the impurities in the electrode, — chiefly iron, — and the zinc. This action may be prevented by amalgamating the zinc electrode. In this process the mercury dissolves the zinc and not the iron, a uniform surface of the former metal being produced.

An interesting experiment due to Ostwald * illustrates the conditions essential to the continuous production of an electric current. Two electrodes, one of amalgamated zinc and the other of platinum, are each immersed in a solution of potassium sulphate, the two solutions being separated by a porous cup. When the two electrodes are connected by means of a wire, no permanent current passes. An inappreciable quantity of zinc goes into solution, since any current must necessarily first liberate potassium at the platinum electrode, the potassium thus set free reacting with the water. This process requires the expenditure of more energy than the solution of the zinc supplies. If sulphuric acid is added to the compartment containing the zinc, the condition of the system will be unchanged, the zinc remaining undissolved. If, on the other hand, a few drops of sulphuric acid are added to the compartment containing the platinum electrode, bubbles of hydrogen will appear and the zinc will dissolve with the simulta-

---

* Phil. Mag. [5], **32**, 145 (1891).

neous development of an electric current. This experiment shows that in order that positively charged ions may enter a solution, an equivalent amount of negatively charged ions must be introduced, or an equivalent amount of positively charged ions must be removed.

Reversible Cells. Galvanic cells are either *reversible* or *non-reversible,* according as the processes taking place within them can be reversed or not. If we disregard the slow processes of diffusion, the Daniell cell may be taken as an example of an almost perfect reversible element. If an electromotive force slightly less than that of the cell be applied to it in the reverse direction, the current within the cell will flow from the zinc to the copper electrode as usual. On the other hand, if the external electromotive force slightly exceeds that of the cell, the current within the cell will flow in the reverse direction, zinc being deposited and copper dissolved.

Any cell from which gas is evolved is non-reversible, since the passage of a current in the reverse direction cannot restore the cell to its original condition.

Relation between Chemical Energy and Electrical Energy. Helmholtz and Thomson were the first to propose a theory of the action of the reversible cell. According to this theory the energy of the chemical process taking place within the cell was considered to be completely transformed into electrical energy. It was soon shown that this theory is inadequate, since, with the exception of the Daniell cell, the chemical energy is not equivalent to the electrical energy produced. Subsequently, Gibbs[*] and Helmholtz[†] showed independently that only in those cells in which the electromotive force does not vary with the temperature, is the chemical energy completely transformed into electrical energy. They also derived an equation expressing the relation between the chemical and electrical energies in any reversible cell. Let us imagine a reversible element in which an amount of heat q, is either liberated or absorbed, when one faraday of electricity has passed through the cell. Let the cell be immersed in a bath, which is so arranged that the temperature of the cell can be maintained constant under any working conditions. If the chemical process within the cell is accompanied by an evolution or an absorption of heat, then of necessity, heat energy must be removed or supplied in order to maintain the temperature of the system constant. It is evident that this will involve a corresponding decrease or increase in the electrical energy produced by the cell. The effect of the evolution or absorption of heat upon the electrical energy of the cell may be derived in the following manner: Let the cell be heated from its initial temperature T to the temperature $(T + dT)$, and let the corresponding change in the electromotive force of the cell be dE. If now the circuit be closed and one faraday of electricity be allowed to pass through the cell, $F\,(E + dE)$ units of electrical work will be done. In order that the temperature of the cell may not change, $(q + dq)$ units of heat must be absorbed. The cell is now cooled to the temperature T, at which the electromotive force of the cell is E, and F units of electricity are sent through the cell in the reverse direction, thus increasing the energy of the cell by FE. In order to maintain the temperature of the cell unchanged, q units of heat must be removed. If the cell is completely reversible, when this cycle of operations is completed, it will be restored to its original condition. The total work done during the cycle is $F\,(E + dE) - FE$, and the amount of heat transformed into work is $(q + dq) - q$; therefore, applying the second law of thermodynamics, we have

---

[*] Proc. Conn. Acad., 3, 501 (1878).

[†] Sitzungsbericht., Ber. Akad., 22, 825 (1882).

$$\frac{dq}{q} = \frac{F\,dE}{q} = \frac{dT}{T},$$

or

$$q = FT\frac{dE}{dT}. \tag{1}$$

Since the electrical energy is equal to FE, the relation between this and Q, the chemical energy of the cell, expressed in calories, becomes

$$FE = Q + q. \tag{2}$$

Substituting in equation (2) the value of q given in equation (1), we obtain

$$F\pi = Q + FT\frac{dE}{dT},$$

or

$$E = \frac{Q}{F} + T\frac{dE}{dT}. \tag{3}$$

When $\frac{d\pi}{dT} = 0$, E becomes equal to $\frac{Q}{F}$, or, when the temperature coefficient of the cell is zero, the electrical energy is equal to the chemical energy. This is true of the Daniell cell, which has an extremely small temperature coefficient.

For cells in which the electromotive force varies appreciably with the temperature, it is possible to calculate the value of the electromotive force at any temperature by means of the Gibbs-Helmholtz equation, provided the temperature coefficient is known. In the Grove gas cell, $E = 1.062$ and $Q = 34{,}200$ calories, hence

$$T\frac{dE}{dT} = 1.062 - \frac{34{,}200}{96{,}540 \times 0.2394} = -0.418.$$

The value determined by direct experiment is − 0.416 volt. The Gibbs-Helmholtz equation shows that the amount of heat accompanying a chemical process does not alone furnish a measure of the electrical energy which may be obtained from it, since the heat which is absorbed from the surrounding medium may also be transformed into electrical energy, or the output of electrical energy may be less than the heat evolved by the chemical reaction within the cell.

Solution Pressure. It is a familiar fact that water has a tendency to assume the form of vapor, and if the vapor be continually removed from its surface, a definite mass of water will gradually be completely transformed into the state of vapor. The pressure of the vapor at any one temperature is a measure of the tendency of water to undergo this transformation. This tendency of water to assume another form than that in which it actually exists, is typical of all substances. Attention has already been directed to this fact in connection with the application of the law of mass action to heterogeneous equilibria. It was then pointed out that all solids have a definite vapor pressure at a definite temperature, which is independent of the amount of solid present. When a solid, such as cane sugar, is brought in contact with water, it tends to pass into solution. This tendency is constant at constant temperature, since the active mass of the solid is constant. From the close analogy between the vapor state and the dissolved state, the tendency of a solid to pass into solution is termed the *solution pressure.* A dissolved solid, on the other hand, also shows a tendency to separate from the solution as the concentration is increased. When the solution becomes supersaturated, the tendency of the solute to separate in the solid form is greater than the tendency of the solid to dissolve. It is evident from these considerations that the pressure exerted by the dissolved solid is its osmotic pressure, and whether the solid will dissolve or separate from the solution depends upon whether the solution pressure is greater or less than the osmotic pressure.

This conception of solution pressure was introduced by Nernst,* and in conjunction with the theory of electrolytic dissociation it has proved of great value in affording a much deeper insight into the mechanism of the development of differences in potential within a galvanic cell. Thus, when a metal is dipped into water it tends to dissolve owing to its solution pressure P and, in consequence of this tendency, it sends a certain number of positive ions into solution. The solution thus becomes positively charged, and the metal, which was initially neutral, acquires a negative charge due to the loss of a certain amount of positive electricity. This process will cease when the solution becomes so strongly charged with positive electricity that it prevents the separation of any more positive ions from the metal. Relatively few ions leave the metal before equilibrium is established, since the charge on each ion is so great; in fact, the concentration of metal ions in the solution is much too small to be detected analytically. When a metal is dipped into a solution of one of its salts, the conditions are altered. In this case, the positive ions of the metal already present in the solution oppose the entrance of more positive ions, and the equilibrium between these two opposing tendencies will be conditioned by the relative values of the solution pressure P, of the metal, and the osmotic pressure p, of the ions of the dissolved salt.

---

* Zeit. phys. Chem., 4, 150 (1889).

It is evident that the three following conditions are possible: —

(1) If $P > p$, the metal will continue to send ions into the solution until the accumulated charges in the solution oppose further action. The solution acquires a positive charge and the metal a negative charge.

(2) If $P < p$, the positive ions of the dissolved salt will separate on the metal until the accumulated charges oppose further action. The metal acquires a positive charge and the solution a negative charge.

(3) If $P = p$, no action will take place and no difference of potential will be established between the metal and the solution. These three cases are represented diagrammatically in Fig. 95.

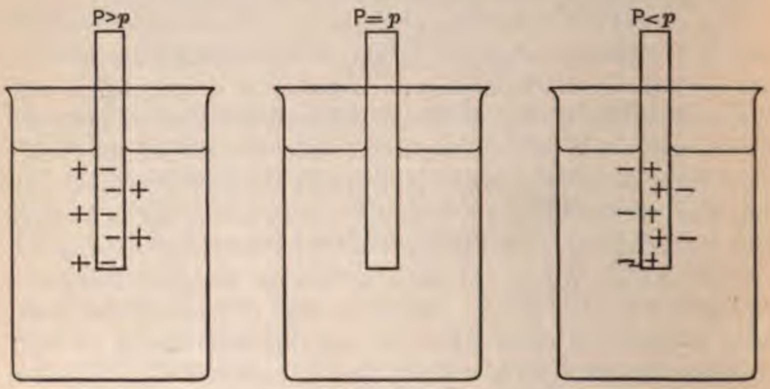


Fig. 95.

When equilibrium is established and the metal is negative against the solution, the metal is surrounded by a layer of positively charged ions. This constitutes what is known as a Helmholtz *electrical double layer*. If positive electricity be communicated to the metal, the double layer will be broken and more ions will pass from the metal into the solution, but as soon as the supply of positive electricity is cut off, the double layer will again be formed. Similarly, when the metal is positive against the solution, an electrical double layer will be formed, the metal being surrounded by a layer of negatively charged ions.

The actual existence of a Helmholtz double layer has been demonstrated by Palmaer.* In his experiments, Palmaer allowed exceedingly minute globules of mercury to fall into a dilute solution of mercurous nitrate contained in a tall vessel, the bottom of which was covered with a layer of pure mercury, as shown in Fig. 96. Since the solution pressure of mercury is less than the osmotic pressure of the $Hg^{\cdot}$ ions, each drop of mercury as it enters the solution will acquire a positive charge, and if the theory of the electrical double layer is correct, this positively charged globule should attract negatively charged ions and drag them down through the solution. When the globule reaches the mercury at

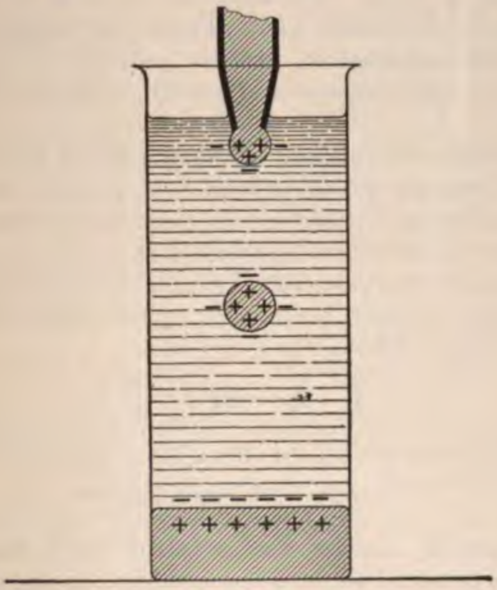


Fig. 96.

---

* Zeit. phys. Chem., 25, 265 (1898); 28, 257 (1899); 36, 664 (1901).

the bottom of the vessel, it will give up its positive charge and as many $Hg^{\cdot}$ ions will pass into solution as there are NO_3' ions in the double layer. The solution will thus become more concentrated just above the layer of mercury on the bottom of the vessel. Palmaer's experiments showed that this difference in concentration is actually produced, in some cases the concentration in the upper part of the solution being reduced as much as 50 per cent.

The metals sodium, potassium, . . . zinc, cadmium, cobalt, nickel, and iron are negative against solutions of their salts, or $P > p$. The noble metals are generally positive against solutions of their salts, or $P < p$. The anions are, so far as is known, positive to solutions of their salts. Electrolytic solution pressure varies with the temperature, with the nature of the solvent, and also with the concentration of the active substance in the electrode.

The Difference of Potential between a Metal and a Solution. From the foregoing considerations, it is possible to derive an equation expressing the difference of potential between a metallic electrode and a solution of one of its salts.

Let us imagine one gram-ion of a metal to be transferred from the electrolytic solution pressure P, to the osmotic pressure p. The osmotic work done will be

$$\int_p^P v\,dp = RT\int_p^P \frac{dp}{p}.$$

Integrating this expression, we have

$$\text{Osmotic work} = RT \log_e \frac{P}{p}.$$

The corresponding electrical energy gained is $nF\pi$, where π is the difference of potential between the metal and the solution, $F = 1$ faraday $= 96{,}540$ coulombs, and n is the valence of the metal. Since the osmotic work done is equivalent to the electrical energy gained, we may equate these two expressions, as follows: —

$$nF\pi = RT \log_e \frac{P}{p},$$

or

$$\pi = \frac{RT}{nF} \log_e \frac{P}{p}. \tag{1}$$

Expressing both sides of equation (1) in electrical units, and transforming to Briggsian logarithms, we obtain

$$\pi = \frac{2}{96{,}540 \times n \times 0.4343 \times 0.2394} T \log \frac{P}{p},$$

or

$$\pi = \frac{0.0002}{n} T \log \frac{P}{p}. \qquad (2)$$

For univalent ions at 17°, we have

$$\pi = 0.0575 \log \frac{P}{p}. \qquad (3)$$

In a galvanic cell composed of two metals, each immersed in a solution of one of its salts, a difference of potential may be established (1) at the junction of the two metals, (2) at the junction of the two solutions, and (3) at the points of contact of the metals with their respective solutions. If the temperature remains constant, (1) is negligible, and in general, (2) is exceedingly small; therefore, the electromotive force of the cell may be considered as due to the differences of potential arising at the two electrodes. Assuming the temperature to be 17°, the electromotive force of the cell will be

$$E = \pi_1 - \pi_2 = \frac{0.0575}{n} \log \frac{P_1}{p_1} - \frac{0.0575}{n} \log \frac{P_2}{p_2}.$$

The Measurement of Electromotive Force. The value of the electromotive force of a cell may vary with the conditions of measurement. Since, according to Ohm's law, $E = C\,(R + r)$, where R is the resistance of the external circuit and r is the internal resistance of the cell, it follows that the fall of potential CR, in the external circuit, will only be equal to E when r is negligible in comparison with R. Furthermore, when the circuit is closed, the electrodes of the cell frequently become polarized, owing to the deposition of the products of electrolysis, and an opposing electromotive force is set up.

To avoid these difficulties, the electromotive force is usually measured on open circuit by the Poggendorff compensation method. In this method the electromotive force to be measured is just balanced by an equal and opposite electromotive force, so that no current passes. The arrangement of the apparatus for such measurements is shown in Fig. 97. If the two ends of the wire *AB*

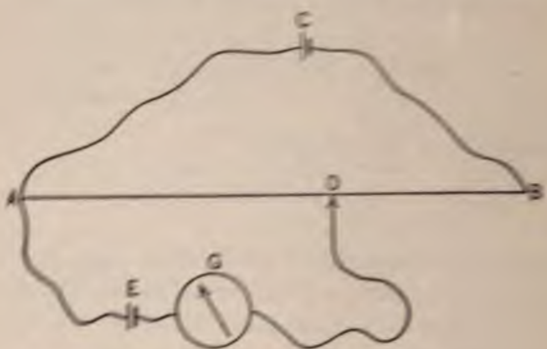


Fig. 97.

of a Wheatstone bridge are connected to a lead accumulator *C*, there will be a uniform fall of potential along its length. The amount of fall along any portion *AD* will be proportional to the length *AD*, and equal to the fraction $\frac{AD}{AB}$ of the total fall of potential along the entire length of the wire. Now let one terminal of a cell whose electromotive force is less than that of *C* be connected to *A*, and the other terminal be connected through a galvanometer *G*, with a sliding contact *D*, the two cells *E* and *C* working in opposition. A current will flow through the circuit *AEGD*, and will be indicated by the galvanometer at all positions, except that at which the fall of potential along the wire from *A* to *D* is equal to the electromotive force of *E*. Hence we have

$$\text{e.m.f. of } C : \text{e.m.f. of } E :: AB : AD,$$

from which the value of the electromotive force of the cell *E*, can be calculated. Since the electromotive force of a lead accumulator is not quite constant, it is customary, after having determined the point *D*, to substitute a standard cell for *E*, and balance this against the accumulator, finding a new point of balance D'. We now have the proportion

$$\text{e.m.f. of } C : \text{e.m.f. of standard} :: AB : AD'.$$

Combining these two proportions, we obtain

$$\text{e.m.f. of } E : \text{e.m.f. of standard} :: AD : AD'.$$

Instead of using a galvanometer as a "null" instrument for indicating when the point of balance has been reached, a capillary electrometer may be employed.

Standard Cells. It is apparent that the accuracy of all measurements of electromotive force is dependent upon the cell employed as a standard. Much time has been devoted to the study of various reversible elements with a view to establishing a standard of electromotive force. As a result, we have the complete specifications for two standard cells, either of which may be readily reproduced.

(a) *The Weston, or Cadmium Standard Cell.* The most widely used standard of electromotive force is the so-called Weston cell, made up according to the scheme

$$\text{Hg} - \text{Solution } Hg_2SO_4 \,\|\, \text{Solution } CdSO_4 - \text{Cd}.$$

A diagram of the usual form of the Weston cell is given in Fig. 98.

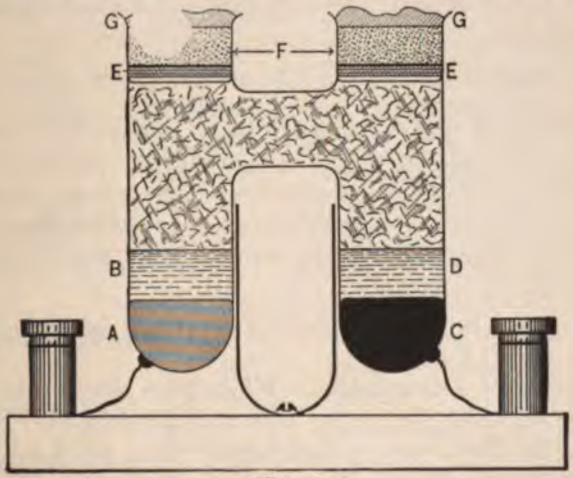


Fig. 98.

A short platinum wire is sealed through the bottom of each limb of the H-shaped vessel. In one limb is placed a small amount of a 10 to 15 per cent cadmium amalgam, *A*; *B* is a layer of small crystals of $CdSO_4 \cdot \frac{8}{3}H_2O$. In the other limb is placed a small amount of pure mercury, over which is a layer, *D*, of a paste composed of solid mercurous sulphate and a saturated solution of cadmium sulphate. The cell is then filled with crystals of cadmium sulphate and a saturated solution of cadmium sulphate. The two limbs of the cell are closed with a thin layer of paraffin *E*, cork *F*, and sealing wax *G*. If carefully prepared, this cell will remain unaltered for years and will have an electromotive force at 20° of 1.0183 volts. In addition to the fact that it can be so easily reproduced, the temperature coefficient of the cell is almost negligible.

The electromotive force of a Weston standard cell at any temperature *t*, is given by the formula

$$\text{e.m.f. at } t^\circ = 1.0183 - 0.000038\,(t - 20).$$

(b) *The Clark, or Zinc Standard Cell.* Until about ten years ago, the Clark cell was considered to be the most trustworthy standard of electromotive force. This cell is made up according to the scheme

$$\text{Hg} - \text{Solution } Hg_2SO_4 \,\|\, \text{Solution } ZnSO_4 - \text{Zn}.$$

The construction of the cell is similar to that of the Weston cell. It may be reproduced with great accuracy and with no more trouble than the Weston cell, but its relatively large temperature coefficient renders it less satisfactory. The electromotive force of the Clark standard cell at any temperature *t*, may be calculated by means of the formula

$$\text{e.m.f. at } t^\circ = 1.4328 - 0.00119\,(t - 15) - 0.00007\,(t - 15)^2.$$

The Capillary Electrometer. When pure mercury is covered with sulphuric acid, its surface tension is diminished. This may be shown by the following experiment: In a small evaporating dish place about 5 cc. of pure mercury, and cover it with a 10 per cent solution of sulphuric acid to which has been added enough potassium dichromate to impart a light yellow color to the solution. The globule of mercury will immediately flatten out, indicating that its surface tension has diminished. If now the mercury be touched with a piece of iron wire, it will instantly contract until the contact with the wire is broken; it will then flatten out, until it again comes in contact with the wire, when the globule of mercury will once more contract. In this way a regular pulsation of the mercury may be obtained. This interesting phenomenon was observed early in the nineteenth century by Henry, but was first satisfactorily explained by Lippmann * in 1873. Lippmann showed that when the globule of mercury is negatively electrified, its surface tension increases and the drop shrinks. If sufficient negative electricity is imparted to the mercury it is possible to restore the globule to its original form. On applying more negative electricity, the globule of mercury again expands. When the iron wire touches the globule it charges it negatively, because when the iron dissolves, it furnishes positively charged ions to the solution and thus acquires a negative charge which it imparts to the mercury. At the same time, the chromic acid in the solution undergoes reduction to chromium sulphate. Lippmann concluded from his experiments that the difference of potential arises at the surface of contact between the mercury and the solution of the electrolyte, and that the surface tension of the mercury is a function of the difference of potential. Making use of this principle he constructed the capillary electrometer, a convenient form of which is shown in Fig. 99. The bulb A, through the bottom of which is sealed a platinum wire, contains pure mercury and dilute sulphuric acid (1 : 6). Pure mercury is poured into the other limb of the electrometer

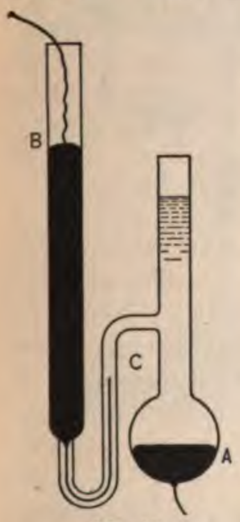


Fig. 99.

---

* Pogg. Ann., 149, 546 (1873).

until it stands at B in that tube, and at C in the capillary tube. Owing to the capillary depression of the mercury, C lies below B. Electrical connection with the mercury at B is established by means of a platinum wire.

The position of the mercury in the capillary is determined by its surface tension; if the surface tension is increased, the mercury will descend; if it is diminished, the mercury will ascend. If a negative charge is communicated to the mercury at B, the surface tension will be increased and the meniscus will descend; if a positive charge is imparted to the mercury at B, the surface tension will be diminished and the meniscus will ascend.

The amplitude of the movement of the meniscus is an inverse function of the diameter of the capillary tube. If the meniscus be observed through a microscope provided with an eye-piece micrometer, Fig. 100, it is possible to detect very slight movements, and to measure differences of potential less than 0.0001 volt.

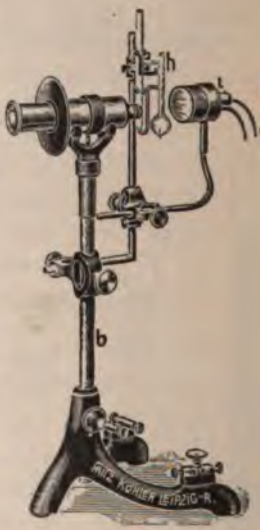


Fig. 100.

The capillary electrometer is an excellent "null" instrument. In using the electrometer no large electromotive force should be applied, since the meniscus surface becomes polarized very easily. If this should occur, a new surface may be secured by blowing gently at B and forcing a drop of mercury out of the capillary into the bulb. Lippmann studied the effect of steadily increasing potentials on the movement of the meniscus. Plotting movements of the meniscus on the axis of ordinates, and potentials on the axis of abscissæ, he found that there is a maximum in the curve corresponding to about 0.8 volt. This is the electromotive force which must be applied in order to counterbalance the difference of potential produced by the contact of dilute sulphuric acid he surface of the mercury. At the meniscus surface an al double layer is formed. The mercury is positively charged, and above it there must be a layer of negatively charged ions, as shown in Fig. 101. Just how this double layer is formed is not known with certainty, but it has been suggested that the slight film of oxide which is probably present on the surface of the purest mercury, dissolves in the sulphuric acid forming a solution of mercurous sulphate, and from this solution the positively charged $Hg^{\cdot}$ ions deposit on the mercury, giving it a positive charge. Whether this explanation is correct or not, the fact remains that the mercury is positive against the solution.

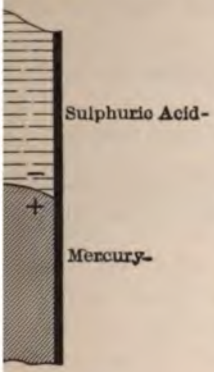


Fig. 101.

nal Electrodes. The method commonly employed for asurement of the difference of potential between a metal solution, is based upon the use of an electrode in which the ace of potential between the electrode and a certain solution of its salts is known. Such an electrode is called a *normal le.* If a cell is made up by combining the normal electrode ne electrode whose potential is to be determined, it is possible, neasurements of the resulting electromotive force, to calthe value of the unknown difference of potential. The most ient electrode to prepare is the normal calomel electrode, a ctory form of which is shown in Fig. 102. The bottom of ctrode vessel is covered with a layer of pure mercury, upon is poured a paste, prepared by rubbing together in a mortar ry and calomel, moistened with a molar solution of potassium le. The vessel is then filled with a molar solution of the salt which has been saturated with calomel by prolonged g with the latter. Connection with the mercury is established by means of a platinum wire sealed into a glass tube *A*, the being passed through the rubber stopper which closes the In using the calomel electrode, the bent side tube *C* is filled with molar potassium chloride by applying suction at the side tube *B*, which is then closed by means of a pinch-cock.

The difference of potential, at any temperature t, of the calomel electrode prepared as described, and represented by the scheme

$$\text{Hg} - \text{Solution HgCl in molar KCl},$$

is

$$\pi = -0.560 \{1 + 0.0006 (t - 18)\} \text{ volt.}$$

The negative sign indicates that the solution is negative to the electrode. In order to measure the potential of another electrode by means of the calomel electrode, the arrangement shown in Fig. 103 is commonly used. Here *A* represents the "half-element" of which the potential is to be determined, *B* represents the side tube of the calomel electrode, and *C* represents an intermediate, connecting vessel containing a molar solution of potassium chloride. In cases where potassium chloride forms a precipitate with the electrolyte in *A*, the solution in *C* may be replaced by a molar

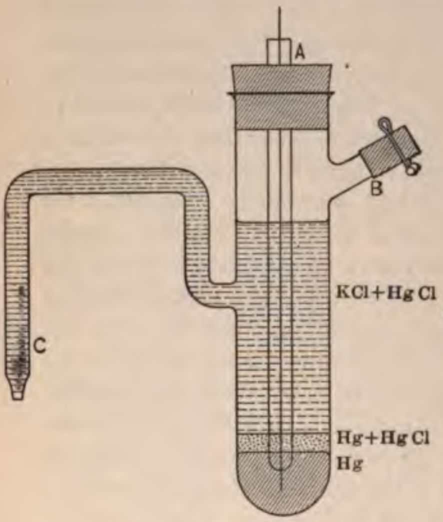


Fig. 102.

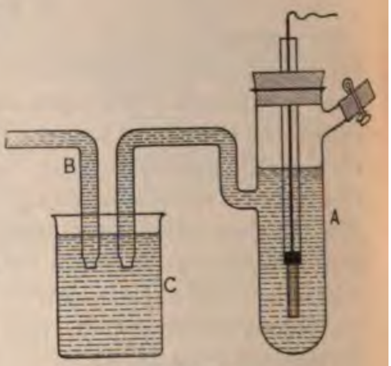


Fig. 103.

solution of potassium nitrate without altering the value of the electromotive force of the cell. The original measurement of the potential of the calomel electrode was made by forming a cell with this and another electrode whose potential against its solution is zero. Such an electrode is known as a *null electrode.* Thus, if a copper electrode is immersed in a solution of copper sulphate, the $Cu^{\cdot\cdot}$ ions will leave the solution and charge the electrode positively. If now a solution of potassium cyanide is added, the nearly undissociated salt, $K_2Cu_2(CN)_4$, will be formed, and by adding a sufficient amount of the solution, the concentration of the $Cu^{\cdot\cdot}$ ions may be reduced until the metal and the solution have the same potential. The addition of more potassium cyanide will still further diminish the osmotic pressure of the $Cu^{\cdot\cdot}$ ions, and the electrode will acquire a negative charge. Similarly, mercury in a solution of a double cyanide may be used as a null electrode.

Another form of null electrode is the so-called *dropping electrode* of Helmholtz.* The principle involved in this electrode has already been discussed in connection with Palmaer's experiment (p. 453). An extremely fine stream of mercury is allowed to flow from a funnel having a minute capillary orifice: the stem of the funnel dips below the surface of a molar solution of potassium chloride containing mercurous ions. As each little globule enters the solution, it acquires a positive charge and attracts the negatively charged ions of the electrolyte, dragging them down with itself. When the globule reaches the layer of mercury at the bottom of the vessel, its surface and capacity are diminished, and as many $Hg^{\cdot}$ ions leave the layer of mercury and enter the solution as there were negatively charged ions carried down by the globule. This process continues until the osmotic pressure of the remaining ions is equal to the solution pressure of the metal: the mercury, both in the stream and at the bottom of the vessel, has the same potential as the solution. If now the difference of potential between the mercury in the funnel and the mercury in the vessel be measured, we shall obtain the potential of mercury against a molar solution of potassium chloride. The dropping electrode was for a long time regarded as an ideal standard of potential, but Nernst has quite recently pointed out a number of serious objections to it. Until a wholly satisfactory standard of potential is obtained, he proposes that the potential of the *hydrogen electrode* be adopted as the standard. This consists of a strip of platinized platinum, half in pure hydrogen gas and half in a solution of sulphuric acid of such concentration that it shall contain 1 gram of hydrogen ions per liter. The use of the hydrogen electrode as a standard is, of course, purely arbitrary, but there are many advantages in referring differences of potential to this standard. Owing to certain experimental difficulties attending the use of this electrode, it is customary to make the actual measurements with the calomel electrode, and then refer them to the hydrogen standard, taking the potential of the calomel electrode to be − 0.283 volt when referred to the hydrogen electrode as zero. *The negative sign indicates that the solution is negative against the electrode.*

---

* Ann. der Phys., **44**, 42 (1890).

Measurement of the Difference of Potential between a Metal and a Solution. The difference of potential between a metal and a solution of one of its salts is easily determined by means of the calomel electrode. For example, in order to determine the potential of zinc against a molar solution of zinc sulphate, the electromotive force E, of the combination

$$\mathrm{Zn} - \mathrm{m\ ZnSO_4} \,||\, \underset{\text{(cal. electrode)}}{\mathrm{m\ KCl,\ HgCl} - \mathrm{Hg}},$$

is measured and found to be 1.08 volts, the mercury being the positive terminal of the cell. Applying the Nernst equation,

$$E = \pi_1 - \pi_2 = \frac{RT}{2F}\log_e\frac{P_1}{p_1} - \frac{RT}{F}\log_e\frac{P_2}{p_2},$$

in which P_1 and p_1 denote the solution pressure and the osmotic pressure of the zinc ions, and P_2 and p_2 denote the solution pressure and the osmotic pressure of the mercury ions, we have

$$1.08 = \frac{RT}{2F}\log_e\frac{P_1}{p_1} - (-0.56),$$

or

$$\frac{RT}{2F}\log_e\frac{P_1}{p_1} = 1.08 - 0.56 = 0.52 \text{ volt.}$$

That is, the zinc electrode is negative against a molar solution of zinc sulphate, the difference of potential being 0.52 volt. As an example of a cell in which the mercury of the calomel electrode is the negative terminal of the cell, we may take the following combination: —

$$\text{Cu} - \text{m CuSO}_4 \,||\, \text{m KCl, HgCl} - \text{Hg.}$$

The electromotive force of this cell is 0.025 volt. Since the current flows from the copper to the mercury, we have

$$E = 0.025 = -0.56 - \frac{RT}{2F}\log_e\frac{P_1}{p_1},$$

or

$$\frac{RT}{2F}\log_e\frac{P_1}{p_1} = -0.025 - 0.56 = -0.585 \text{ volt.}$$

That is, the copper electrode is positive against a molar solution of copper sulphate. From the above results it is possible to calculate the electromotive force of the combination

$$\text{Zn} - \text{m ZnSO}_4 \,||\, \text{m CuSO}_4 - \text{Cu.}$$

Since, according to Nernst's equation

$$E = \pi_1 - \pi_2 = \frac{RT}{2F}\log_e\frac{P_1}{p_1} - \frac{RT}{2F}\log_e\frac{P_2}{p_2},$$

where P_1 and p_1 refer to the zinc, and P_2 and p_2 refer to the copper, we have

$$E = 0.52 - (-0.585) = 1.105 \text{ volts.}$$

Concentration Elements. We now proceed to consider cells in which the electromotive force depends primarily on differences in concentration, — the so-called "concentration elements."

Concentration elements may be conveniently divided into two classes: (a) *elements in which the electrodes are of different concentrations, and* (b) *elements in which the solutions are of different concentrations.*

(a) *Elements in which the Electrodes are of Different Concentrations.* (*Amalgams and Alloys.*) If in the equation

$$E = \frac{RT}{nF}\log_e\frac{P_1}{p_1} - \frac{RT}{nF}\log_e\frac{P_2}{p_2},$$

$p_1 = p_2$, as is the case when the ionic concentrations of the two solutions are identical, then we have

$$E = \frac{RT}{nF}\log_e\frac{P_1}{P_2},$$

where P_1 and P_2 are the respective solution pressures of the metal dissolved in the electrodes. If the amalgams are dilute, the osmotic pressure of the dissolved metal will be proportional to the solution pressure of the electrode, and since osmotic pressure is proportional to concentration, we may replace P_1 and P_2 in the above formula by the proportional terms, c_1 and c_2, the respective concentrations of the metal in the two electrodes. Hence, we have

$$E = \frac{RT}{nF}\log_e\frac{c_1}{c_2}.$$

The accuracy of this equation has been fully established by the experiments of Meyer,* and Richards and Forbes.†

Meyer's results for zinc amalgams in solutions of zinc sulphate are given in the accompanying table.

T, degrees.	c_1	c_2	E (obs.).	E (calc.).
284.6	0.003366	0.00011305	0.0419	0.0416
291.0	0.003366	0.00011305	0.0433	0.0425
285.4	0.002280	0.0000608	0.0474	0.0445
333.0	0.002280	0.0000608	0.0520	0.0519

The agreement between the observed and calculated values of E is all that can be desired. That the above formula holds for zinc amalgams may be considered as a proof of the fact that the zinc dissolves in the mercury as monatomic molecules. Thus, suppose the zinc to be present in the mercury in the form of diatomic molecules; then while the electrical energy would be equal to $2\,FE$, the osmotic work required to develop this energy would be $\frac{1}{2} RT \log_e \frac{c_1}{c_2}$, hence we should have

---

* Zeit. phys. Chem., **7**, 477 (1891).

† Publication of the Carnegie Institution, No. 56.

$$E = \frac{1}{2}\frac{RT}{2\,F} \log_e \frac{c_1}{c_2},$$

or the calculated value of the electromotive force would be just one-half of the observed value. The mercury in the amalgam has been shown to exert no effect upon the electromotive force of the cell so long as the dissolved metal has the greater potential.

(b) *Elements in which the Solutions are of Different Concentrations.* In this type of cell we have two electrodes of the same metal immersed in solutions of different ionic concentrations of the metal. Hence, we may put $P_1 = P_2$ in the equation

$$E = \frac{RT}{nF} \log_e \frac{P_1}{p_1} - \frac{RT}{nF} \log_e \frac{P_2}{p_2},$$

which then takes the form

$$E = \frac{RT}{nF} \log_e \frac{p_1}{p_2}.$$

Since osmotic pressure is proportional to concentration, p_1 and p_2 may be replaced by the proportional terms c_1 and c_2, and the foregoing equation becomes

$$E = \frac{RT}{nF} \log_e \frac{c_1}{c_2},$$

or

$$E = \frac{RT}{nF} \log_e \frac{m_1\alpha_1}{m_2\alpha_2},$$

where m_1 and m_2 are the molar concentrations of the two solutions and α_1 and α_2 are the corresponding degrees of ionization. As an example of a concentration element of this class we may take the following: —

$$\mathrm{Ag} - 0.01\ \mathrm{m\ AgNO_3} \,\|\, 0.1\ \mathrm{m\ AgNO_3} - \mathrm{Ag}.$$

The degrees of ionization of the two solutions at 18° are as follows: — for 0.01 m $AgNO_3$, $\alpha = 0.93$, and for 0.1 m $AgNO_3$, $\alpha = 0.81$. Substituting in the equation

$$E = 0.058 \log \frac{m_1\alpha_1}{m_2\alpha_2},$$

we have

$$E = 0.058 \log \frac{0.1 \times 0.81}{0.01 \times 0.93} = 0.0545 \text{ volt.}$$

The value of E found by direct experiment is 0.055 volt.

In the example just given, the electrodes are reversible with respect to the positive ion of the electrolyte. Such electrodes are known as *electrodes of the first type.* It is also possible to construct cells with electrodes which are reversible with respect to the negative ion of the electrolyte. These are termed *electrodes of the second type.* The calomel electrode is an example of an electrode of this latter type. If positive electricity passes from the metal to the solution, the mercury combines with the Cl' ions forming mercurous chloride, and if positive electricity passes in the reverse direction, chlorine dissolves and mercurous chloride is formed. In other words the electrode behaves like a chlorine electrode, giving up or absorbing the element according to the direction of the current. A typical combination involving an electrode of the second type is the following: —

$$Ag - 0.1 \text{ m } AgNO_3 - KNO_3 - 0.1 \text{ m } KCl, AgCl - Ag.$$

This particular combination was studied by Goodwin * with a view to determining the solubility of silver chloride. If we assume a saturated solution of silver chloride to be completely ionized, then the solubility product will be

$$c_{Ag^{\cdot}} \times c_{Cl'} = s.$$

Since the concentrations of the two ions, $Ag^{\cdot}$ and Cl', are equal, it follows that $\sqrt{s}$ will be equal to the solubility of the silver chloride. The electromotive force of a concentration cell at 25° is given by the equation

$$E = \frac{0.0595}{n} \log \frac{m_1\alpha_1}{m_2\alpha_2},$$

---

* Zeit. phys. Chem., 13, 577 (1894).

or

$$\log \frac{m_1\alpha_1}{m_2\alpha_2} = \frac{En}{0.0595}.$$

The value of E at 25° for the above cell was found to be 0.450 volt. The degrees of ionization of the two electrolytes are as follows: — for 0.1 molar $AgNO_3$, $\alpha = 0.82$, and 0.1 molar KCl, $\alpha = 0.85$. Substituting in the preceding equation, we obtain

$$\log \frac{0.1 \times 0.82}{c_2} = \frac{0.450}{0.0595},$$

therefore,

$$c_2 = 2.24 \times 10^{-9}.$$

Or, 1.94×10^{-9} is the concentration of the $Ag^{\cdot}$ ion in mols per liter in a 0.1 molar potassium chloride solution of silver chloride. Hence the solubility product s will be

$$s = 2.24 \times 10^{-9} \times 0.085 = 1.91 \times 10^{-10},$$

and

$$\sqrt{s} = 1.38 \times 10^{-5};$$

that is, the solubility of silver chloride in a saturated aqueous solution is 1.28×10^{-5} mol per liter at 25°.

The Difference of Potential at the Junction of the Solutions of Two Electrolytes. Thus far we have not taken into consideration the potential differences which may be established at the junction of two solutions. Nernst * has shown that in many cases it is possible to calculate these differences of potential by means of his osmotic theory of the origin of electromotive force, and the values obtained are in close agreement with the results of experiment. Let us imagine that two solutions of hydrochloric acid of different concentrations are brought together so as to avoid mixing, the acid in each solution being highly ionized. The hydrogen and chlorine ions will diffuse independently, and since the former move with the greater velocity, the more dilute solution will soon contain an excess of $H^{\cdot}$ ions and the more concentrated solution an excess of Cl' ions. The more dilute solution will become positively charged owing to the presence of an excess of $H^{\cdot}$

---

* Zeit., phys. Chem., 4, 129 (1889).

ions, while the more concentrated solution will acquire a negative charge due to the presence of an excess of Cl′ ions. The accumulation of positive electricity, however, will retard the velocity of the H˙ ions and accelerate the velocity of the Cl′ ions, so that ultimately the two ions will move with the same velocity. The difference of potential produced in this way will cease to exist when the two solutions have acquired the same concentration.

In general, it may be stated that the difference of potential set up at the junction of the two solutions is caused by the difference in the rates of migration of the two ions, the more dilute solution acquiring a charge corresponding to that of the faster moving ion.

Electromotive Force of Concentration Cells with Transference. Let u and v be the migration velocities of the cation and the anion respectively, and let p_1 be the osmotic pressure of the ions in the concentrated solution and p_2 the osmotic pressure of the ions in the dilute solution. Now let one faraday of electricity pass through the two solutions, the current entering on the concentrated side; then $\frac{u}{u+v}$ gram-equivalents of positive ions will migrate from the concentrated to the dilute solution, while $\frac{v}{u+v}$ gram-equivalents of negative ions will migrate from the dilute to the concentrated solution. The maximum work done by the process will be

$$\frac{u}{u+v}RT\log_e\frac{p_1}{p_2}-\frac{v}{u+v}RT\log_e\frac{p_1}{p_2}=\frac{u-v}{u+v}RT\log_e\frac{p_1}{p_2}.$$

The corresponding electrical energy developed is πF, hence we have

$$\pi=\frac{u-v}{u+v}\cdot\frac{RT}{F}\log_e\frac{p_1}{p_2},$$

or, since osmotic pressure is proportional to concentration, we may substitute c_1 and c_2 for p_1 and p_2 in the preceding equation, and obtain the following expression for the electromotive force at the junction of the two solutions: —

$$\pi=\frac{u-v}{u+v}\cdot\frac{RT}{F}\log_e\frac{c_1}{c_2}.$$

As an example of the use of the above formula, we may take the calculation of the electromotive force of the following combination: —

$$Ag \underset{(a)}{-} 0.1\text{ m } AgNO_3 \underset{(b)}{-} 0.01\text{ m } AgNO_3 \underset{(c)}{-} Ag.$$

Taking the junctions (a), (b), and (c) in order, we obtain

$$E = \frac{RT}{F}\log_e\frac{C}{c_1} + \frac{u-v}{u+v}\cdot\frac{RT}{F}\log_e\frac{c_1}{c_2} - \frac{RT}{F}\log_e\frac{C}{c_2}$$
$$= \frac{2\,v}{u+v}\cdot\frac{RT}{F}\log_e\frac{c_2}{c_1}.$$

But $\frac{2\,v}{u+v} = n_a$, the transport number of the anion, and therefore we may write the preceding equation in the form

$$E = 2\,n_a\frac{RT}{F}\log_e\frac{c_2}{c_1}. \qquad (1)$$

Assuming the temperature to be 17° and passing to Briggsian logarithms, we have

$$E = 0.116\,n_a\log\frac{c_2}{c_1}.$$

The transport number for the anion of silver nitrate is 0.522, while $c_1 = m_1\alpha_1 = 0.1 \times 0.82 = 0.082$, and $c_2 = m_2\alpha_2 = 0.01 \times 0.94 = 0.0094$. Hence,

$$E = -2 \times 0.522 \times 0.058 \times \log\frac{0.082}{0.0094},$$

or

$$E = -0.057 \text{ volt}.$$

The value found by direct experiment is −0.055 volt.

It is to be noted that if the electromotive force at the junction of the two solutions is negative, equation (1) takes the form

$$E = 2\,n_c\frac{RT}{F}\log_e\frac{c_2}{c_1},$$

where n_c is the transport number of the cation.

Electromotive Force of Concentration Cells without Transference. A less familiar type of concentration cell is that which does not involve transference. The following combination may be taken as an example of such a cell: —

$$\mathrm{Ag} \mid \underset{c_1}{\mathrm{AgCl,\ KCl}} \mid \mathrm{K\,(Hg)}_x \parallel \mathrm{K\,(Hg)}_x \mid \underset{c_2}{\mathrm{KCl,\ AgCl}} \mid \mathrm{Ag}.$$

It will be observed that this cell is in reality made up of two independent cells and involves no liquid junction. While the elimination of diffusion appreciably simplifies the theoretical treatment of cells of this type, practically it is difficult to find electrodes which are reversible toward both ions of the electrolyte. The passage of one faraday of electricity through the cell results in the formation on the dilute side of one equivalent of potassium chloride from the silver chloride and the amalgam, while on the concentrated side a corresponding amount of potassium chloride is decomposed. If we assume the solutions to be so dilute as to be completely ionized, one equivalent of potassium chloride will function as two mols of gas, and the electromotive force of the cell will be

$$E = \frac{2\,RT}{F} \log_e \frac{c_2}{c_1}. \qquad (2)$$

Formulas for the Difference of Potential at Liquid Junctions. As has been pointed out, the total electromotive force of a concentration cell with transference is made up of the algebraic sum of the potentials at the two electrodes and the potential at the junction of the two solutions. Since the value of the potential at the electrodes alone is often desired, numerous formulas have been derived for the calculation of the potential at the liquid junction.

In addition to the formula of Nernst, already mentioned, formulas have been proposed by Planck,* Henderson,† Cumming,‡ Lewis and Sargent,§ and MacInnes.|| Of these different formulas that of MacInnes possesses distinct advantages.

---

* Wied. Ann., **40**, 561 (1890).

† Zeit. phys. Chem., **59**, 118 (1906); **63**, 325 (1908).

‡ Trans. Faraday Soc., **8**, 86 (1912); **9**, 174 (1913).

§ Jour. Am. Chem. Soc., **31**, 363 (1909).

|| Ibid., **37**, 2301 (1915).

If one faraday of electricity be passed through the cell

$$\mathrm{Ag} \mid \underset{c_1}{\mathrm{AgCl, KCl}} \mid \underset{c_2}{\mathrm{KCl, AgCl}} \mid \mathrm{Ag},$$

one equivalent of chloride ions will enter the dilute solution while a corresponding amount will be electrolyzed out of the more concentrated solution. The current will be carried across the liquid junction by the migration of n_c equivalents of potassium ions in the direction of the current and by the migration of $(1 - n_c)$ equivalents of chloride ions in the opposite direction. The total effect of the passage of one faraday of electricity will be the transference of one equivalent of salt from the more concentrated to the more dilute solution. The osmotic work at the junction of the two solutions will correspond to the algebraic sum of the number of ion equivalents which have migrated from the concentrated to the dilute solution, or $n_c - (1 - n_c) = 2\,n_c - 1$.

In order to obtain the electrical energy necessary to perform this amount of osmotic work, let us consider the following cell involving no transference: —

$$\mathrm{Ag} \mid \underset{c_1}{\mathrm{AgCl, KCl}} \mid \mathrm{K\,(Hg)}_x \parallel \mathrm{K\,(Hg)}_x \mid \underset{c_2}{\mathrm{KCl, AgCl}} \mid \mathrm{Ag}.$$

The passage of one faraday of electricity through this cell involves, as we have seen, the formation of one equivalent each of potassium and chloride ions in the dilute solution, and the removal of one equivalent of each ion from the more concentrated solution. The electrical energy accompanying the transfer of two ion equivalents from one solution to the other will be equal to the product of the electromotive force of the cell and one faraday, or EF.

The electromotive force π, at the liquid junction, can now be obtained by the simple proportion

$$EF : \pi F = 2 : 2\,n_c - 1,$$

or

$$\pi = \frac{E\,(2\,n_c - 1)}{2}. \tag{1}$$

Since the ratio of E_t, the electromotive force of the cell with transference, to E, the electromotive force of the cell without transference, is equal to n_c, it follows that equation (1) may be written in the form

$$\pi = \frac{E_t\,(2\,n_c - 1)}{2\,n_c} = E_t\,(1 - 1/2n_c). \tag{2}$$

It is to be observed that equations (1) and (2) involve no assumptions concerning the concentrations of the ions in the solutions, one of the characteristics which distinguishes these formulas from any of the others hitherto proposed.

Lewis and Sargent * have proposed a modification of a formula derived by Planck for the difference of potential at the junction of two equally concentrated electrolytes having a common ion. If Λ_1 and Λ_2 are the equivalent conductances of the two electrolytes, the value of the liquid junction potential π is given by the formula

$$\pi = \frac{RT}{F} \log_e \frac{\Lambda_1}{\Lambda_2}. \tag{3}$$

The junction between two different concentrations of two electrolytes with a common ion may be replaced by two junctions, one of which connects two different concentrations of the same electrolyte, and the other connects two different electrolytes of the same concentration. For example, the junction

0.1 N NaCl | 0.05 N HCl

may be replaced by

0.1 N NaCl | 0.05 N NaCl | 0.05 N HCl
(A) (B)

in which the potential of the junction (A) may be calculated by equations (1) or (2) and the potential of junction (B) by equation (3).

The electromotive force at the junction of solutions of differently concentrated uni-univalent ionogens which do not contain a common ion may, in like manner, be calculated by employing three junctions. Thus, the junction

0.1 N KNO_3 | 0.05 N NaCl

---

* Loc. cit.

may be replaced by

$$0.05\text{ N NaCl}\mid\underset{(A)}{}0.1\text{ N NaCl}\mid\underset{(B)}{}0.1\text{ N KCl}\mid\underset{(B')}{}0.1\text{ N KNO}_3.$$

The potential at (A) may be calculated by means of equations (1) or (2) and the potentials at (B) and (B′) by means of equation (3).

By the use of equations (1), (2), and (3) in the manner indicated, it is possible to calculate the junction-potential between the solutions of any two uni-univalent ionogens to within a few tenths of a millivolt.

Normal Electrode Potential. The difference of potential at a reversible electrode, when the concentration of the ions of the electrolyte is normal, is known as the *normal electrode potential.*

According to Nernst, the expression for the difference of potential at a single electrode is

$$\begin{aligned}\pi &= \frac{RT}{nF}\log_e\frac{P}{p}\\ &= \frac{RT}{nF}\log_e\frac{C}{c},\end{aligned} \qquad (1)$$

where P is the solution pressure of the electrode, p is the osmotic pressure of the ions of the electrolyte, and where C and c are concentrations proportional to P and p respectively. If the concentration of the ions is unity, $c = 1$, and the expression for the normal electrode potential E_0 becomes

$$E_0 = \frac{RT}{nF}\log_e C. \qquad (2)$$

On subtracting (1) from (2), we obtain

$$E_0 = \pi + \frac{RT}{nF}\log_e c, \qquad (3)$$

where c is the concentration of the ions in a solution whose electrode potential is π. In the actual determination of normal electrode potentials, the value of c in equation (3) is usually very much less than unity.

The following table gives the most important electrode potentials, the data in the second column being referred to the normal calomel electrode as zero, and the data of the third column being referred to the normal hydrogen electrode as zero.

NORMAL ELECTRODE POTENTIALS.

Electrode.	N. E. Potential, N. Calomel Electrode = 0.	N. E. Potential, N. Hydrogen Electrode = 0.
Cations.		
Copper	+0.046	+0.329
Hydrogen	−0.283	+0.000
Lead	−0.412	−0.129
Mercury	+0.467	+0.750
Platinum	+0.580 ca.	+0.863 ca.
Potassium	−3.48	−3.20
Silver	+0.515	+0.718
Sodium	+2.998	+3.281
Tin	−0.475	−0.192
Zinc	−1.053	−0.770
Anions.		
Bromine	+0.797	+1.08
Chlorine	+1.067	+1.35
Iodine	+0.345	+0.628
Oxygen	+0.110	+0.393

It should be observed that the value of the normal electrode potential cannot be calculated directly by means of equation (2) owing to the uncertainty attaching to the quantity *C*. In fact the best interpretation that we have of the physical significance of *C* is, that it is a quantity whose logarithm is proportional to the normal electrode potential.

Electrometric Determination of Valence. The equation of Nernst for the electromotive force of a concentration cell may be employed to determine the valence of the ions.

For example, the chemical behavior of mercurous salts is such as to justify the use of single or double formulas involving either $Hg^{\cdot}$ or $Hg_2^{\cdot\cdot}$. To determine which of these two formulas is correct, Ogg * set up the following cell: —

$$Hg \mid \begin{matrix} 0.5\ N\ \text{Mercurous Nitrate} \\ 0.1\ N\ HNO_3 \end{matrix} \parallel \begin{matrix} 0.05\ N\ \text{Mercurous Nitrate} \\ 0.1\ N\ HNO_3 \end{matrix} \mid Hg$$

---

* Zeit. phys. Chem., 27, 285 (1898).

and found its electromotive force at 17° to be 0.029 volt. If we neglect the difference of potential at the junction of the two solutions, the electromotive force of this cell may be calculated by the familiar formula

$$E = \frac{RT}{nF}\log_e\frac{c_2}{c_1}.$$

Assuming that c_2/c_1 is equal to 10, and passing to Briggsian logarithms, we have

$$0.029 = 0.058/n,$$

or

$$n = 2.$$

Hence the valence of the mercurous ion is 2 and it must, in consequence, be represented by $Hg_2^{\cdot\cdot}$. It follows that the correct formula of mercurous nitrate is $Hg_2(NO_3)_2$.

Electrometric Determination of Transport Numbers. The formula for the electromotive force of a concentration cell with transference has been shown to be

$$E_t = \frac{2\,n_cRT}{nF}\log_e\frac{c_2}{c_1}. \qquad (1)$$

If the electromotive force of such a combination is measured and the values of c_1 and c_2 are accurately known, obviously the value of the transport number of the cation n_c, can be calculated. If, after having measured E_t, a similar cell without transference be set up and its electromotive force measured, it is possible to obtain an expression for n_c which does not involve either c_1 or c_2. As has been shown, the electromotive force of a cell without transference, E, is given by the formula

$$E = \frac{2\,RT}{nF}\log_e\frac{c_2}{c_1}. \qquad (2)$$

Dividing equation (1) by equation (2), we obtain

$$n_c = \frac{E_t}{E}, \qquad (3)$$

which expression gives the transport number in terms of the two measured electromotive forces. This method for the determination of transport numbers was first suggested by Helmholtz.*

The transport number of the lithium ion has recently been determined in this manner by Pearce and Mortimer * using cells made up according to the following schemes: —

---

* Ges. Abhl. I, 840: II, 979.

$$\mathrm{Ag} \mid \mathrm{AgCl}, \underset{c_1}{\mathrm{LiCl}} \parallel \underset{c_2}{\mathrm{LiCl}}, \mathrm{AgCl} \mid \mathrm{Ag} \quad \text{(with transference)},$$

$$\mathrm{Ag} \mid \mathrm{AgCl}, \underset{c_1}{\mathrm{LiCl}} \mid \mathrm{Li\,(Hg)}_x \parallel \mathrm{Li\,(Hg)}_x \mid \underset{c_2}{\mathrm{LiCl}}, \mathrm{AgCl} \mid \mathrm{Ag} \left(\begin{matrix}\text{without}\\ \text{transference}\end{matrix}\right).$$

A comparison between their results and the values given by Kohlrausch and Holborn † is afforded by the accompanying table.

Concentration Ratio	1.0–0.1	0.5–0.05	0.1–0.01	0.05–0.005
Mean n_c (K. and H.)	0.285	0.300	0.340	0.360
Mean n_c (P. and M.)	0.279	0.322	0.343	0.365

It will be observed that the agreement between the two series of results is satisfactory.

Concentration and Activity. If in the equation for the electromotive force of a concentration cell without transference, viz.,

$$E = \frac{2\,RT}{nF} \log_e \frac{c_2}{c_1},$$

we substitute the observed value of E and solve the equation for the ratio, c_2/c_1, we find that the value thus obtained does not agree with the value derived from conductance measurements. In other words, if m_1 and m_2 are the actual molar concentrations of the two solutions forming the cell, and α_1 and α_2 are the corresponding degrees of ionization, we find that the ratio $m_2\alpha_2/m_1\alpha_1$ is not equal to the ratio c_2/c_1 as calculated from the electromotive force of the cell. This is shown by the following table which gives the ratios of the ionic concentrations of solutions of potassium chloride corresponding to various ten-to-one salt concentrations.

RATIOS OF ION CONCENTRATIONS IN SOLUTIONS OF POTASSIUM CHLORIDE.

Concentration Ratio.	c_2/c_1 (Conductance).	c_2/c_1 (Electromotive Force).
0.5 : 0.05	8.85	8.09
0.1 : 0.01	9.16	8.33
0.05 : 0.005	9.30	8.64
0.01 : 0.001	9.62	9.04

---

* Jour. Am. Chem. Soc., **40**, 518 (1918).

† Leitvermögen der Elektrolyte, p. 201.

If the values of c_2/c_1 in the table are plotted as ordinates against the higher concentration of each pair of solutions as abscissæ, we obtain the curves shown in Fig. 104. It will be seen that notwithstanding the fact that the ratios differ widely when calculated by the two methods, both sets of figures approach the limiting value, 10, at infinite dilution. From this it is evident that the equation of Nernst is only applicable to cells involving solutions which are practically infinitely dilute.

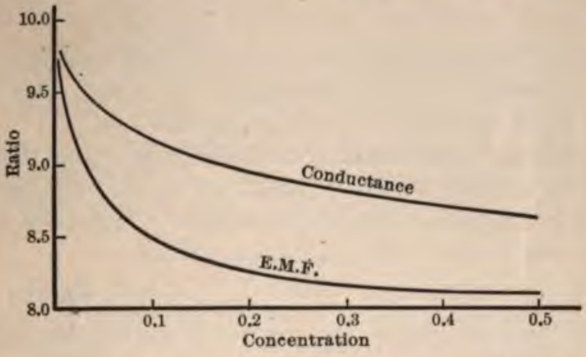


Fig. 104.

The figures in the last column of the table are known as *activity ratios*, and the individual values of c_1 and c_2 are termed *activities*. If it be assumed that in 0.001 KCl the activity of the ions is identical with their concentration, as obtained by multiplying the total concentration of the salt by the ionization as determined from the conductance ratio, then the activities in 0.01 N KCl and 0.1 N KCl can be calculated. The values so obtained are given in the following table together with the corresponding values of the ionization calculated, (1) from the conductance ratio, and (2) from the so-called "thermodynamically effective" ionization, this latter being the quotient obtained by dividing the activity by the corresponding total concentration.

That the degree of ionization determined from conductance measurements does not agree with the value obtained from measurements of electromotive force has been known for some time.

ACTIVITY AND IONIZATION OF POTASSIUM CHLORIDE SOLUTIONS.

Salt Concentration.	Activity.	Λ/Λ_0.	"Thermodynamically Effective" Ionization.
0.001 N	0.000979	97.9	(97.9)
0.01 N	0.00885	94.1	88.5
0.1 N	0.0738	86.1	73.8

It is thought that the decrease in activity of the ions with increasing concentration is due to a change in the nature of the solvent brought about by the electric charges on the ions.

Electrometric Determination of Hydrolysis. One of the most satisfactory methods which we possess for the determination of the degree of hydrolysis of salts depends upon the measurement of the electromotive force of cells made up as follows: —

$$\mathrm{Pt_{H_2}} \mid \text{salt solution} \mid \text{sat. } \mathrm{NH_4NO_3}\,^* \parallel \mathrm{N\ KCl,\ Hg_2Cl_2} \mid \mathrm{Hg}.$$

From the measured electromotive force of the cell, the concentration of the hydrogen ion in the solution can be determined, and from this the degree of hydrolytic dissociation of the salt can be calculated. The method is especially valuable in cases where the concentration of the hydrogen ion is very small. Unfortunately the application of the method is restricted to the salts of metals less noble than hydrogen. In other words, it cannot be used to determine the hydrolysis of the salts of metals which would be precipitated upon the platinum electrode. The applicability of the method is further limited by the fact that certain ions, such as $Fe^{\cdot\cdot\cdot}$, NO_3', and ClO_3', are either wholly or partially reduced by the hydrogen of the hydrogen electrode.

The method has been successfully applied by Denham † to the determination of the hydrolysis of various salts, among which may be mentioned, aluminium chloride, aluminium sulphate, nickel chloride, nickel sulphate, cobalt sulphate, and ammonium chloride.

As an illustration of the method we may take the case of ammonium chloride which dissociates hydrolytically according to the equation

---

* A saturated solution of ammonium nitrate is interposed between the solutions to eliminate any difference of potential at the junction of the solutions.

† Jour. Chem. Soc., **93**, 41 (1908); Zeit. anorg. Chem., **57**, 361 (1908).

$$NH_4Cl + H{\cdot}OH \rightleftarrows NH_4OH + HCl.$$

Here we have a weak base and a very strong acid as the products of hydrolytic dissociation. While the ammonium hydroxide may be regarded as practically non-ionized, the hydrochloric acid is to be considered as having undergone complete ionization. If one mol of ammonium chloride is dissolved in v liters of water and the degree of hydrolytic dissociation is x, then the concentrations of the products of the reaction, ammonium hydroxide and hydrochloric acid, will be x/v. Since the acid is completely ionized, x/v will also represent the concentrations of the hydrogen and chloride ions. Assuming that the active mass of the water remains constant, we have, according to the law of mass action,

$$K_h = \frac{x^2}{v\,(1 - x)},$$

where K_h is the hydrolytic constant. Since v is known, it only remains to determine x/v, or the concentration of the hydrogen ions, in order to be able to calculate K_h. The potential at the hydrogen electrode is given by the familiar formula

$$\pi = \frac{RT}{nF} \log_e \frac{c_{H^{\cdot}}}{C},$$

or denoting the normal electrode potential $RT \log_e C$ by π_0, we may write

$$\pi = \pi_0 + \frac{RT}{nF} \log_e \frac{x}{v}.$$

According to Denham, the electromotive force of the cell,

$$\longleftarrow$$

$$Pt_{H_2} \mid N/32\ NH_4Cl \mid \text{sat. } NH_4NO_3 \parallel N\ KCl,\ Hg_2Cl_2 \mid Hg,$$

at 25° is 0.6056 volt, the current flowing outside the cell in the direction of the arrow. The potential of the normal calomel electrode being $+ 0.56$ volt, it follows that the potential of the hydrogen electrode, $\pi = 0.56 - 0.6056 = - 0.0456$ volt. Therefore,

$$- 0.0456 = \pi_0 + \frac{RT}{nF} \log_e \frac{x}{v}.$$

The absolute value of the potential of the normal hydrogen electrode π_0, referred to the normal calomel electrode as + 0.56 volt and *not as zero,* is + 0.277 volt. Substituting this value in the foregoing equation and passing to Briggsian logarithms, we have

$$0.059 \log \frac{x}{v} = 0.0456 - 0.277 = -0.2314.$$

Solving this equation we find $x/v = 0.340 \times 10^{6}$ gram-ions of hydrogen per liter. Since the value of x/v would be $\frac{1}{32}$ if the salt were completely hydrolyzed, the percentage of hydrolysis under the conditions of the experiment, *i.e.*, when $v = 32$, is

$$\frac{0.340 \times 10^{6} \times 100}{1/32} = 0.0108.$$

The value of the hydrolytic constant is given by the equation

$$K_h = \frac{(0.340 \times 10^{6})^2}{32\,(1 - 0.340 \times 10^{6})} = 0.31 \times 10^{9}.$$

The degree of hydrolytic dissociation of ammonium chloride has been determined by Noyes from measurements of electrical conductance. The value of x for 0.01 N NH_4Cl was found by him to be 0.02 at 18°, while Denham found $x = 0.018$ at 25° by extrapolation of his electrometric data.

Oxidation and Reduction Elements. When a dissolved substance passes from a lower to a higher state of oxidation, the change in the positive ion may be considered as due to an increase in the number of electrical charges on the ion; thus, when a ferrous salt is oxidized to the ferric state, the change may be represented by the equation

$$\mathrm{Fe}^{\cdot\cdot} + (+) \rightarrow \mathrm{Fe}^{\cdot\cdot\cdot}.$$

Similarly, the reduction of a ferric salt to the corresponding ferrous salt may be represented by the reverse equation, or

$$\mathrm{Fe}^{\cdot\cdot\cdot} \rightarrow \mathrm{Fe}^{\cdot\cdot} + (+).$$

The formation of zinc ions from metallic zinc may be considered as an oxidation, and may be represented by the equation

$$\mathrm{Zn} + 2\,(+) \rightarrow \mathrm{Zn}^{\cdot\cdot}.$$

The formation of negative ions from a non-metallic element may be considered as a reduction, as for example, the change of potassium ferricyanide to potassium ferrocyanide, which may be represented by the equation

$$\mathrm{Fe(CN)_6'''} + (-) \rightarrow \mathrm{Fe(CN)_6''''}.$$

The foregoing considerations lead to the following definition of the terms oxidation and reduction: *Oxidation is the process in which a substance takes up positive or parts with negative charges, and reduction is the process in which a substance takes up negative or parts with positive charges.*

The potential difference between a metal and a solution of one of its salts is a measure of the tendency of the metal to form ions, or in other words is the criterion of its tendency towards oxidation. The tendency of an ion in a lower state of oxidation to pass over into a higher state of oxidation may be determined by means of electromotive force measurements.

A typical oxidation cell is the following: —

$$\mathrm{Pt - Fe^{\cdot\cdot} \parallel Fe^{\cdot\cdot\cdot} - Pt}.$$

If the platinum electrodes are connected to a lead accumulator, and a current is passed in the direction of the arrow

$$\overset{+}{\mathrm{Pt}} - \underrightarrow{\mathrm{Fe^{\cdot\cdot} \parallel Fe^{\cdot\cdot\cdot}}} - \mathrm{Pt},$$

the ferrous ions on one side of the element will all be oxidized to the ferric state, while the ferric ions on the other side will all be reduced to the ferrous state, thus:

$$\overset{+}{\mathrm{Pt}} - \mathrm{Fe^{\cdot\cdot\cdot} \parallel Fe^{\cdot\cdot}} - \overset{-}{\mathrm{Pt}}.$$

If now the connection with the accumulator is broken and the two platinum electrodes are connected with a wire, the following process will take place: — ferric ions will give up positive charges to one electrode, thereby being reduced to ferrous ions, while the charges given up pass along the wire to the other electrode, there converting some ferrous ions to ferric ions. This process will continue until an equilibrium is established, in which the ratio

$Fe^{\cdot\cdot} : Fe^{\cdot\cdot\cdot}$ will be the same in both solutions. The electromotive force corresponding to this change gives a measure of the tendency of the ions to undergo oxidation, and is directly proportional to the ionic concentrations.

The following modification of the Nernst equation gives the relationship between ionic concentrations and the resulting electromotive force: —

$$E_{(c_o \rightarrow c_i)} = P + \frac{RT}{nF} \log_e \frac{c_o}{c_i},$$

where $E_{(c_o \rightarrow c_i)}$ is the electromotive force produced by the passage from the lower, or "ous" state of oxidation to the higher, or "ic" state of oxidation; P is the potential when the concentrations of the "ous" and "ic" ions are equal, c_o and c_i are the ionic concentrations of the lower and higher states of oxidation respectively, and n is the difference in valence of the two kinds of ions. A number of oxidation and reduction elements have been studied by Bancroft.*

Heat of Ionization. If the difference of potential between a metal and the solution of one of its salts is known, together with its temperature coefficient, it is possible to calculate the heat of ionization of the metal by means of the Gibbs-Helmholtz equation,

$$\pi = \frac{Q}{nF} + T\frac{d\pi}{dT}.$$

Solving the equation for Q, the heat evolved when one mol of ions is formed at the electrode, we have

$$Q = \left(\pi - T\right)\frac{d\pi}{dT}nF.$$

For example, the potential of zinc against a molar solution of zinc chloride is -0.497 volt at 25°, and the temperature coefficient of electromotive force is 0.000664 volt per degree. Substituting in the equation, we have

$$Q = [-0.497 - (273 + 25) \times 0.000664]\,(2 \times 96{,}540 \times 0.2394)$$

or $Q = 32{,}120$ calories.

---

* Zeit. phys. Chem., 10, 387 (1892).

t is, the heat of the reaction

$$Zn + 2\,(+) \rightarrow Zn^{\cdot\cdot}$$

20 calories per mol of zinc.

Cells. It is interesting to note that gases may function trodes in much the same way as metals or amalgams. Gas des are usually prepared by partially sing strips of platinized platinum in tion of a suitable electrolyte, and ng the gas through the solution until tant difference of potential is estab- between it and the electrode. A very ctory form of gas electrode is shown in 05. Reference has already been made hydrogen electrode in connection the measurement of single electrode tials.

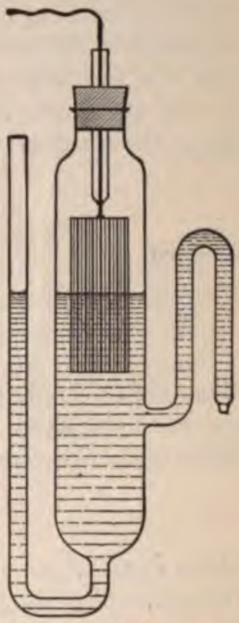


Fig. 105.

s electrode is completely reversible haves like a plate of metallic hydro- the reaction at the electrode being ented by the equation

$$H_2 + 2\,(+) \rightleftarrows 2\,H^{\cdot}.$$

mount of energy developed by the ge of a certain quantity of gas into nic state is precisely the quantity nec- and sufficient to produce the reverse l.

s being true, the metal of the electrode can exert no influence the electromotive force. A hydrogen concentration cell formed by connecting two hydrogen electrodes, containing s at different pressures, through an intermediate electrolyte. irection of the current is such that the pressures on the two of the cell tend to become equal, molecular hydrogen being d on the high pressure side, and ionized hydrogen being dis- ed on the low pressure side.

electromotive force of such a cell can be calculated by means of the Nernst equation. Let us consider a cell composed of two hydrogen electrodes, each at atmospheric pressure, the H˙ ion concentration in each being c_1, then

$$E = \frac{RT}{2F}\log_e\frac{C_1}{c_1} - \frac{RT}{2F}\log_e\frac{C_1}{c_1} = 0,$$

where C_1 is the molecular concentration of the hydrogen dissolved in the platinum at atmospheric pressure p_1. Since the hydrogen is present in the form of diatomic molecules, $n = 2$.

If now the pressure of the gas at one electrode be increased to p_2, and the corresponding molecular concentration of the hydrogen in the electrode be C_2, then we shall have

$$E = \frac{RT}{2F}\log_e\frac{C_1}{c_1} - \frac{RT}{2F}\log\frac{C_2}{c_1},$$

or since

$$C_1 : C_2 :: p_1 : p_2,$$

$$E = \frac{RT}{2F}\log_e\frac{p_1}{p_2}. \qquad (1)$$

Equation (1) applies equally well to cells in which two different gases are employed. If solution pressures be used in the calculation of the electromotive force of a gas cell, equation (1) becomes

$$E = \frac{RT}{F}\log_e\frac{P_1}{P_2}, \qquad (2)$$

where P_1 and P_2 are the solution pressures of the two gases. Since the values of E obtained by equations (1) and (2) must be equal, we may write

$$\frac{RT}{2F}\log_e\frac{p_1}{p_2} = \frac{RT}{F}\log_e\frac{P_1}{P_2},$$

and

$$\frac{1}{2}\log_e\frac{p_1}{p_2} = \log_e\frac{P_1}{P_2};$$

therefore

$$\frac{p_1}{p_2} = \frac{P_1^2}{P_2^2}.$$

That is, the ratio of the actual gas pressures is equal to the ratio of the squares of the corresponding solution pressures.

Ionization of Water. An important application of the gas cell is its use in determining the degree of ionization of water. If we measure the electromotive force of the cell

$$Pt_{H_2} - 0.1\text{ m NaOH} - 0.1\text{ m HCl} - Pt_{H_2},$$

and determine the concentration of the $H^{\cdot}$ ions on one side and the concentration of the OH' ions on the other side, we can calculate the concentration of the $H^{\cdot}$ ions in the sodium hydroxide solution. The reaction which produces the current is represented by the equation

$$NaOH + HCl = NaCl + H_2O,$$

or more correctly

$$H^{\cdot} + OH' = H_2O.$$

At 25° the electromotive force of the above cell is 0.646 volt. At the junction of the two solutions an electromotive force of 0.0468 volt is set up; hence the true electromotive force of the cell is $0.646 + 0.0468 = 0.6928$ volt. The degree of ionization of a 0.1 molar solution of hydrochloric acid is $\alpha_1 = 0.924$, and the degree of ionization of a 0.1 molar solution of sodium hydroxide is $\alpha_2 = 0.847$. Introducing these values into the Nernst equation

$$E = \frac{RT}{nF}\log_e\frac{c_1}{c_2},$$

we have

$$0.6928 = 0.0595 \log\frac{0.1 \times 0.924}{c_2}.$$

Solving this equation for c_2, the concentration of the $H^{\cdot}$ ions in the sodium hydroxide solution, we find c_2 to be equal to 1.66×10^{-13}. Therefore

$$s = c_{H^{\cdot}} \times c_{OH'} = 1.66 \times 10^{-13} \times 0.1 \times 0.847 = 1.406 \times 10^{-14},$$

and

$$c_{H^{\cdot}} = c_{OH'} = \sqrt{s} = \sqrt{1.406 \times 10^{-14}} = 1.187 \times 10^{-7}.$$

This value is in excellent agreement with the values obtained from measurements of the electrical conductance of water and the speed of hydrolysis of esters. The values of the degree of ionization of water at 25°, as determined by these three methods, are as follows: —

Electrical conductance of pure water........	1.05×10^{-7}
Velocity of hydrolysis of methyl acetate	1.2×10^{-7}
E.M.F. of hydrogen-oxygen cell.............	1.18×10^{-7}

When we consider the exceedingly small extent to which water is ionized, the close agreement between these results is most satisfactory. The correctness of these figures can be further checked by taking the values of the degree of ionization of water at two temperatures, and calculating the heat of the reaction

$$H^{\cdot} + OH' = H_2O,$$

by means of van't Hoff's isochore equation.

Thus according to Kohlrausch, the degree of ionization of water is 0.35×10^{-7} at 0°, and 2.48×10^{-7} at 50°. Introducing these values into the equation

$$q = \frac{R \times 2.3026 (\log K_2 - \log K_1)\, T_1 T_2}{T_1 - T_2},$$

and solving for q, we obtain 13,810 calories, a value agreeing well with that found by the direct measurement of the heat of neutralization of completely ionized acids and bases, *viz.*, 13,700 calories.

Storage Cells or Accumulators. Storage cells or accumulators, as the name implies, are devices for the storage of electrical energy in the form of chemical energy. Any reversible cell may be employed as an accumulator. Thus, the oxygen-hydrogen cell

$$Pt_{O_2} - \text{Solution of Sulphuric Acid} - Pt_{H_2}$$

may be used as an accumulator, if the gases resulting from the electrolysis of water are collected at the electrodes and then used to produce a current. Practically, the lead accumulator is used almost exclusively. If two lead plates are immersed in a 20 per cent solution of sulphuric acid, a minute amount of lead sulphate will be formed on the surface of each plate. If now a current of electricity is passed through the solution, the lead sulphate on the cathode will undergo reduction to metallic lead, and the lead sulphate on the anode will be oxidized to lead peroxide. In this way we form the cell

$$Pb - 20 \text{ per cent Sol. } H_2SO_4 - PbO_2,$$

the electromotive force of which is about 2 volts. The amounts of lead and lead peroxide produced in this way are so small that the cell can only furnish a very small amount of electrical energy. In order to increase its capacity, the electrodes should be given as large an amount of surface as possible. This may be brought about by the method of Planté, in which the solution is electrolyzed first in one direction and then in the other, thus causing the plates to become spongy; or by the method of Faure, in which a lead "grid" is charged with a paste of lead oxide and red lead, and is then introduced into the solution and the current passed until we obtain spongy lead at the cathode and lead peroxide at the anode. If now the charging circuit is broken and the two electrodes are connected by a wire, a current will flow from the peroxide plate to the lead plate, lead sulphate being slowly formed at each. In charging the accumulator, the lead sulphate on the negative electrode is reduced to metallic lead, the reaction being represented by the following equation: —

$$PbSO_4 + 2\,(-) = Pb^{\cdot\cdot} + SO_4''.$$

At the positive electrode SO_4'' ions are liberated and they react with the lead sulphate and the water of the electrolyte in the following manner: —

$$PbSO_4 + 2\,H_2O + SO_4'' + 2\,(+) = PbO_2 + 4\,H^{\cdot} + 2\,SO_4''.$$

When the cell is discharged SO_4'' ions are liberated at the lead plate forming lead sulphate, as shown by the equation

$$Pb + SO_4'' + 2\,(+) = PbSO_4.$$

At the peroxide plate $H^{\cdot}$ ions are discharged and, in the presence of the electrolyte, convert the lead peroxide into lead sulphate, according to the equation

$$PbO_2 + 2\,H^{\cdot} + H_2SO_4 + 2\,(-) = PbSO_4 + 2\,H_2O.$$

Combining the foregoing equations, we obtain the following single equation summarizing the chemical changes involved in the production of the current: —

$$PbO_2 + Pb + 2\,H_2SO_4 \rightleftarrows 2\,PbSO_4 + 2\,H_2O.$$

The upper arrow represents the reaction on discharging, while the lower arrow represents the reaction on charging.

The electromotive force of the storage cell is approximately 2 volts. It is not completely reversible, but under favorable conditions its efficiency is about 90 per cent; that is, 90 per cent of the electrical energy supplied to it in charging can be recovered on discharging.*

PROBLEMS.

1. Calculate the heat of amalgamation of cadmium at 0° from the following data: — the electromotive force of a cell made up of a 1-per cent cadmium amalgam in a solution of cadmium sulphate is 0.06836 volt at 0°, and 0.0735 volt at 24°.45. *Ans.* 510 calories per mol of Cd.

2. The electromotive force of the cell

$$Pb - 0.01\ m\ Pb(NO_3)_2 - \text{sat. } NH_4NO_3 - m\ KCl,\ HgCl - Hg$$

is − 0.469 volt at 25°. The lead nitrate is 62 per cent ionized. What is the potential of lead against a solution containing 1 mol of Pb ions per liter, referred to the calomel electrodes as zero?

Ans. − 0.405 volt.

3. Calculate the electromotive force of the cell

$$\text{Cu amalgam (a)} - \text{Solution } CuSO_4 - \text{Cu amalgam (b)},$$

at 20°.8, having given that the concentrations of the amalgams (a) and (b) are 0.0004472 and 0.00016645 respectively. *Ans.* 0.0125 volt.

4. Calculate the electromotive force of the cell

$$Cu - m\ CuSO_4 - 0.01\ m\ CuSO_4 - Cu,$$

at 25°, having given the following values for the degree of ionization of the two solutions: — for m copper sulphate, $\alpha_1 = 0.21$, and for 0.01 m copper sulphate, $\alpha = 0.61$. The electromotive force at the junction of the two solutions may be neglected. *Ans.* 0.0458 volt.

---

* For a thorough treatment of the theory of the lead accumulator the student is recommended to consult "Die Theorie des Bleiaccumulators" by F. Dolezalek.

For a detailed account of the primary cells in common use the reader will find Carhart's "Primary Batteries" most satisfactory.

5. At 25° the electromotive force of the cell

$$\text{Zn} - 0.5\text{ m ZnSO}_4 - 0.05\text{ m ZnSO}_4 - \text{Zn}$$

is 0.018 volt. Neglecting the potential developed at the junction of the solutions, and assuming the dilute solution of zinc sulphate to be ionized to the extent of 35 per cent, find the degree of ionization of the concentrated solution. *Ans.* 0.142.

6. What is the electromotive force of the cell

$$\text{Zn} - 0.1\text{ m ZnSO}_4 - 0.01\text{ m ZnSO}_4 - \text{Zn},$$

at 18°? For $ZnSO_4$, $\frac{v}{u+v} = 0.601$, for 0.1 molar $ZnSO_4$, $\alpha = 0.39$, and for 0.01 molar $ZnSO_4$, $\alpha = 0.63$. *Ans.* 0.078 volt.

7. The electromotive force of the cell

$$\text{Ag} - 0.001\text{ m AgNO}_3 - \text{m KNO}_3 - \text{m KI, AgI} - \text{Ag}$$

is 0.22 volt at 18°. A molar solution of KI is 78 per cent ionized, and a 0.001 molar solution of $AgNO_3$ is 98 per cent ionized. Calculate the solubility of AgI. *Ans.* 3.53×10^{-8} mols per liter.

8. The potential of zinc against a solution containing one mol of Zn ions is 0.493 volt, at 18°. Assuming complete dissociation, calculate the solution pressure of zinc in atmospheres.

9. The electromotive force of the Daniell cell

$$\text{Cu} - \text{CuSO}_4 - \text{ZnSO}_4 - \text{Zn}$$

is 1.0960 volt at 0°, and 1.0961 volt at 3°. Calculate the heat of the reaction taking place in the cell. *Ans.* 51,070 calories.

10. Calculate the electromotive force of the cell

$$\text{Pt}_{\text{H}_2} - 0.1\text{ m KOH} - \text{m HCl} - \text{Pt}_{\text{H}_2},$$

at 25°, having given that 0.1 molar KOH is 85 per cent ionized and molar HCl is 70 per cent ionized. *Ans.* 0.757 volt.

CHAPTER XXI.

ELECTROLYSIS AND POLARIZATION.

Polarization. If a difference of potential of about 1 volt is applied to two platinum electrodes immersed in a concentrated solution of hydrochloric acid, it will be found that the current which passes at first, steadily diminishes and ultimately becomes zero. The cessation of the current has been shown to be due to the accumulation of hydrogen on the cathode and chlorine on the anode, these two gases setting up an opposing electromotive force called the *electromotive force of polarization.*

If in the above case the applied electromotive force is increased to 1.5 volts, the counter electromotive force is no longer sufficient to reduce the current to zero. In fact, at any voltage above 1.35 volts a continuous current passes; this is termed the *decomposition potential* of hydrochloric acid.

At all voltages above the decomposition potential, the current C may be calculated by means of the formula

$$E - e = CR,$$

where E is the applied electromotive force, e the counter electromotive force, and R the resistance of the electrolyte.

As the applied electromotive force and the current increase, the polarization increases, since the gases are liberated under a pressure greater than that of the atmosphere; but since the gases escape from the solution the value of e can never become equal to E. The decomposition potential of an electrolyte can be determined in two different ways, *viz.*: (1) by gradually raising the applied electromotive force E until it exceeds e, when the current will suddenly increase; or (2) by charging the electrodes up to atmospheric pressure by means of an electromotive force greater than e, and then breaking the external circuit and measuring the counter electromotive force.

The arrangement of apparatus for the measurement of the electromotive force of polarization, as suggested by Le Blanc,* is indicated in Fig. 106. *A* is the cell in which polarization occurs, *B* is the source of external electromotive force, *C* is a capillary electrometer, *D* is a source of variable potential, and *E* is one prong of an electrically-driven tuning fork which serves to make and break contact with the points *F* and *G* in rapid alternation. When the tuning fork makes contact at *F* the polarizing current flows through *A*, polarizing the electrodes; when contact is made at *G*, the counter electromotive force due to this polarization causes a current to flow through *D* and *C*. The counter electromotive force is balanced by varying *D*, until *C* indicates zero current: the potential of *D* is then equal to the electromotive force of polarization. Just as the electromotive force of a galvanic cell is due to the combined action of several differences of potential, so also the electromotive force of polarization is due to the individual differences of potential located at the electrodes. The method employed for the measurement of polarization at a single electrode was devised by Fuchs, and is illustrated diagrammatically in Fig. 107. Into the vessel containing the electrolyte, dip the

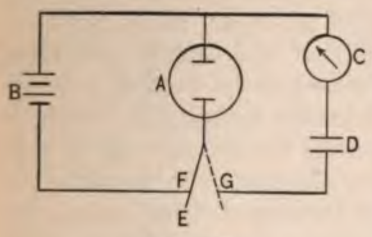


Fig. 106.

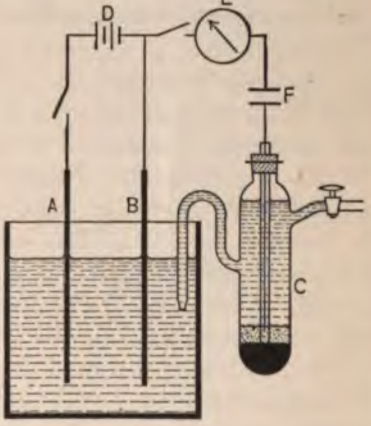


Fig. 107.

---

* Zeit. phys. Chem., 5, 469 (1890).

two electrodes A and B, and the side tube of the calomel normal electrode C. D is the source of external electromotive force, E is a capillary electrometer, and F is a source of variable potential. Before closing the external circuit DAB, the potential of the electrode B against the solution is first measured. Then the circuit DAB is closed, thereby polarizing the electrode B. The external circuit is again broken and the potential of B against the solution remeasured. The difference between the final and initial values of the electrode potential gives the polarization at B. In like manner, the polarization at the electrode A can be measured. The small amount of electricity which is necessary to polarize an electrode is termed the *polarization capacity of the electrode.* This factor is dependent upon the extent of surface of the electrode, and also upon the nature of the metal of which the electrode is made. For electrodes of equal surface, the polarization capacity of palladium is greater than that of platinum, when hydrogen is liberated on each. The solubility of hydrogen is greater in palladium than in platinum, and consequently, because a larger amount of hydrogen is dissolved, a greater quantity of electricity will be required to bring the pressure of the hydrogen up to that of the hydrogen dissolved in the platinum. If, through the processes of solution or diffusion, or through chemical action, the substance which causes the polarization is removed, the electrode is said to be *depolarized.* Thus, when a reducing agent, such as ferrous chloride, is electrolyzed, the oxygen liberated at the anode immediately combines with the electrolyte, forming ferric chloride and preventing polarization of the electrode.

If water be electrolyzed between platinum electrodes, the cathode becomes saturated with hydrogen and the anode with oxygen, until, when the electromotive force of polarization becomes equal to that of the external circuit, the current ceases. The two gases, hydrogen and oxygen, are soluble, however, and consequently diffuse away from the electrodes, either escaping from the solution or recombining to form water. In order to compensate for this continuous loss of gas at the electrodes, a small current continues to flow, thus maintaining the initial electromotive force constant. This small current is termed the *residual current.*

If oxygen is bubbled over the surface of the cathode during electrolysis, the hydrogen is removed as rapidly as it is liberated. Such an electrode on which no new substance is formed during electrolysis is called an *unpolarizable electrode.*

Decomposition Potentials. The decomposition potential of an electrolyte can be determined, as has already been pointed out, by immersing two platinum electrodes in the solution and connecting with a source of electricity, the electromotive force of which can be varied at will. The voltage is gradually increased and the corresponding current is observed. The current increases at first and then drops almost to zero every time the voltage is raised, until the decomposition potential is reached. Beyond this point the current is directly proportional to the electromotive force. If the applied electromotive forces are plotted as abscissæ and the corresponding currents as ordinates, we obtain curves of the form shown in Fig. 108. Some of the decomposition potentials of molar solutions determined by Le Blanc * are given in the accompanying tables.

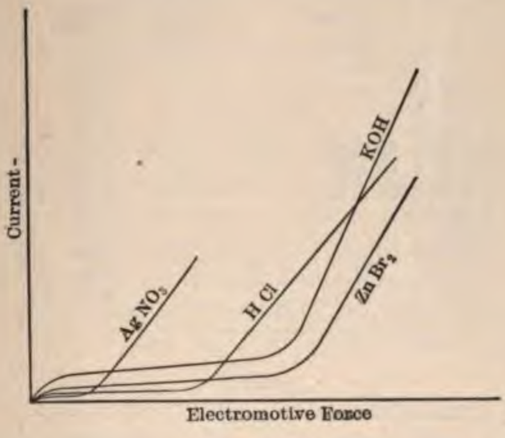


Fig. 108.

---

* Zeit. phys. Chem., 8, 299 (1891).

SALTS.

Salt.	Decomp. Potential.	Salt.	Decomp. Potential.
	Volts.		Volts.
$ZnSO_4$	2.35	$Cd(NO_3)_2$	1.98
$ZnBr_2$	1.80	$CdSO_4$	2.03
$NiSO_4$	2.09	$CdCl_2$	1.88
$NiCl_2$	1.85	$CoSO_4$	1.92
$Pb(NO_3)_2$	1.52	$CoCl_2$	1.78
$AgNO_3$	0.70		

ACIDS.

Acid.	Decomp. Potential.
	Volts.
H_2SO_4	1.67
HNO_3	1.69
H_3PO_4	1.70
$CH_2Cl.COOH$	1.72
$CHCl_2.COOH$	1.66
$CH_2(COOH)_2$	1.69
$HClO_4$	1.65
HCl	1.31
$(COOH)_2$	0.95
HBr	0.94
HI	0.52

BASES.

Base.	Decomp. Potential.
	Volts.
$NaOH$	1.69
KOH	1.67
NH_4OH	1.74

It will be observed that while there is considerable variation in the decomposition potentials of salts, there is very little variation in the decomposition potentials of acids and bases. There is a maximum value of about 1.70 volts to which many acids and bases closely approximate. It is found that all acids and bases which decompose at 1.70 volts give off hydrogen and oxygen at the electrodes. Those acids and bases which decompose at potentials less than the maximum, do not liberate hydrogen and oxygen. When their solutions are sufficiently diluted, however, hydrogen and oxygen are evolved and the decomposition potential rises to the maximum value. Thus, Le Blanc found the following values for the decomposition potential of different dilutions of hydrochloric acid.

Concentration.	Decomp. Potential.
	Volts.
2 m HCl	1.26
$\frac{1}{2}$ m HCl	1.34
$\frac{1}{6}$ m HCl	1.41
$\frac{1}{16}$ m HCl	1.62
$\frac{1}{32}$ m HCl	1.69

When 2 m hydrochloric acid is electrolyzed, hydrogen and chlorine are given off at the electrodes, whereas when the concentration of the acid is reduced to 1/32 m, hydrogen and oxygen are the products of electrolysis, and the decomposition potential increases to 1.70 volts. It is found that the values of the decomposition potentials vary slightly with the nature of the electrodes used. The above values were determined with platinum electrodes.

The Theory of Polarization. Our knowledge of the process taking place at the electrodes during electrolysis is largely due to the investigations of Le Blanc. He determined the electromotive force of polarization at each electrode, varying the external electromotive force from zero up to the decomposition potential of the solution. When the decomposition value was reached, he found the potential of the electrode against the solution to be the same as the difference of potential between the solution and the element liberated at the electrode. Thus, the decomposition potential of a molar solution of zinc sulphate is 2.35 volts; the corresponding difference of potential between the electrode and the solution is found to be 0.493 volt. If a piece of pure zinc is immersed in a molar solution of zinc sulphate, the difference of potential is found to be 0.493 volt, the metal being negative to the solution. It frequently happens that the electrode exhibits the potential due to the deposited metal before the decomposition point of the solution is reached. For example, in a molar solution of silver nitrate the electrode acquires the potential of pure silver in molar silver nitrate before the decomposition value, 0.70 volt, is reached. This is due to the negative solution pressure of the silver which causes the deposition of the ions of the metal without the application of any external electromotive force. When an indifferent electrode, such as platinum, is immersed in a solution of a salt, a very small amount of ionic deposition must occur, otherwise, according to the Nernst equation, an infinite electromotive force must be established. Thus, in the equation

$$\pi = \frac{RT}{nF} \log_e \frac{P}{p},$$

if the solution pressure $P = 0$, it is evident that $\pi = \infty$ and a perpetual motion must result. We are thus forced to the conclusion that when an indifferent electrode is immersed in a salt solution, ions will continue to separate upon it until the tendency for the deposited metal to go back into solution in the ionic state exactly counterbalances the tendency to separation. Hence, the electrode will become positive toward the solution. The magnitude of this difference of potential will be dependent upon the amount of metal deposited. It is to be noted that this difference of potential need not be equal to that between the massive metal and the solution. If the electrodes be connected with an external source of electromotive force, the value of which can be varied at will, and a small electromotive force be applied, more metal will separate on the cathode. This will cause an increase in the solution pressure P, tending to offset further deposition. A still further increase in the external electromotive force will cause the deposition of more metal, and as a result of the corresponding increase in P, further deposition at that voltage will be prevented. Ultimately, when the applied electromotive force is such that P acquires its maximum value, equivalent to that of the massive metal, continuous deposition will occur. An exactly analogous process takes place at the anode. If a gas is liberated, its concentration steadily increases until the maximum pressure is reached, when it will escape from the solution. When strong currents are employed, P does not remain constant, as has been assumed above, but gradually diminishes causing the difference of potential at the electrode to increase.

From the above considerations it becomes clear why a definite electromotive force is necessary to bring about a continuous decomposition of an electrolyte: this will only take place when the concentrations of the substances separating at the electrodes have attained their maximum values. When the decomposition point is reached, the electrode exhibits the potential characteristic of the massive metal. It is evident from the behavior of silver nitrate and the salts of other metals having negative solution pressures, that the maximum values of concentration at the the electrodes need not necessarily be attained simultaneously.

When the products of electrolysis are gaseous, the value of the decomposition potential depends upon the nature of the electrodes. Thus, the cell

$$\mathrm{Pt_{H_2}} - \mathrm{m\ H_2SO_4} - \mathrm{Pt_{O_2}}$$

gives an electromotive force of 1.07 volts if platinized platinum electrodes are used. If an external electromotive force slightly greater than 1.07 volts be applied to this cell in the reverse direction, water will be steadily decomposed, hydrogen and oxygen being evolved at the electrodes. If on the other hand, the platinized electrodes are replaced by electrodes of polished platinum, the decomposition potential rises to 1.68 volts. The reverse electromotive force of polarization, however, is only 1.07 volts. That is, the liberation of gas at a polished platinum electrode is an irreversible process. The difference in the behavior of the two electrodes is explicable when it is remembered that platinum is capable of occluding large amounts of gas. A platinized electrode absorbs the liberated gas very slowly, and when thoroughly saturated, if it is not entirely immersed in the solution, it gradually gives up the gas by diffusion, no bubbles being formed. Thus, if the external electromotive force be raised to 1.07 volts, the system will be in equilibrium, while if the applied electromotive force be greater or less than the equilibrium value, a current will flow in one direction or the other, gas being either liberated or dissolved. In other words, the cell is completely reversible.

Where polished platinum or gold electrodes are used, however, the decomposition potential is, as has been stated, 1.68 volts. Polished electrodes have relatively small absorbing power. Hence, if an electromotive force between 1.07 and 1.68 volts be applied, the gases cannot diffuse away from the electrode rapidly enough, and, when the solution in the vicinity of the electrodes becomes saturated with gas, the current ceases to flow.

A very slow process of diffusion from the solution into the air is constantly taking place however, and this permits the continuous evolution of an exceedingly small amount of gas, while a correspondingly small current traverses the solution.

In order to produce a steady electrolysis, it is necessary to raise the external electromotive force to such an intensity that it is able to bring about the formation of bubbles at the surface of the electrodes. This calls for the expenditure of an amount of work depending upon the condition of the electrode surfaces, the surface tension of the solution, and various other factors. In cases where bubbles are formed, a portion of the available energy of the chemical process is not expended in effecting electrical separation; consequently the reverse electromotive force is less than the applied, and the system is irreversible.

The reactions at the electrodes are catalytically accelerated by the metal of which the electrodes are made. Thus, platinized platinum is the most effective catalyst for the reaction represented by the equation

$$H_2 + 2\,(+) \rightleftarrows 2\,H^{\cdot}.$$

Hydrogen is liberated on platinized platinum at the potential 0 volt, on polished platinum at 0.09 volt, and on zinc at 0.70 volt. The electromotive force necessary to overcome the resistance of the chemical reaction at an electrode is termed the *overvoltage*. Thus, we say that hydrogen is liberated on polished platinum with an overvoltage of 0.09 volt, and on zinc with an overvoltage of

0.70 volt. The following table gives the overvoltage necessary for the liberation of hydrogen and oxygen on electrodes of different metals.

ELECTRODE OVERVOLTAGES.

Hydrogen Liberation.		Oxygen Liberation.	
Metal.	Overvoltage.	Metal.	Overvoltage.
Pt (platinized)	0.00	Au	1.75
Au	0.01	Pt (polished)	1.67
Fe (in NaOH)	0.08	Pd	1.65
Pt (polished)	0.09	Cd	1.65
Ag	0.15	Ag	1.63
Ni	0.21	Pb	1.53
Cu	0.23	Cu	1.48
Pd	0.46	Fe	1.47
Sn	0.53	Pt (platinized)	1.47
Pb	0.64	Co	1.36
Zn	0.70	Ni (polished)	1.35
Hg	0.78	Ni (spongy)	1.28

Primary Decomposition of Water in Electrolysis. The decomposition potential of an electrolyte giving off hydrogen and oxygen at the electrodes, is dependent upon the concentrations of the two ions, $H^{\cdot}$ and OH', and is independent of the nature of the electrolyte. As has already been stated, the decomposition potential of all acids and bases giving off hydrogen and oxygen approximates to 1.70 volts. According to the law of mass action, the product of the concentrations of the $H^{\cdot}$ and OH' ions is constant and independent of the other substances which may be present; hence, although the potentials of the individual electrodes may differ considerably, their sum remains practically constant.

Excluding solutions of salts which undergo reduction by hydrogen, and solutions of chlorides, bromides, and iodides reducible by oxygen, the ions $H^{\cdot}$ and OH', according to Le Blanc, are to be regarded as the sole factors in the electrolysis of solutions, and not the ions of the dissolved electrolyte. In other words, *electrolysis involves a primary decomposition of water.*

The electrical conductance of the solution is due to the ions of the electrolyte together with the ions of water, but at the electrode that process takes place which involves the expenditure of the minimum amount of energy, and this is, under ordinary conditions the separation of the $H^{\cdot}$ and OH' ions.

Thus, when a solution of potassium sulphate is electrolyzed, only a moderately strong current being used, it is not rational to assume the discharge of the $K^{\cdot}$ and SO_4'' ions at the electrodes, and then subsequent reaction between these discharged ions and water. This may be made clear by considering the process taking place at the cathode. According to the explanation based upon so-called "secondary action," the $K^{\cdot}$ ions give up their positive charges to the electrode and then react with water as indicated by the equation

$$K + H^{\cdot} + OH' \rightarrow K^{\cdot} + OH' + H.$$

This explanation involves the transfer to the potassium atom of the positive charge of the $H^{\cdot}$ ion of water; this can only take place if the $H^{\cdot}$ ion holds its charge less tenaciously than the $K^{\cdot}$ ion. Hence, if the $H^{\cdot}$ ion parts with its charge more readily than the $K^{\cdot}$ ion, the former will be discharged primarily at the cathode. Similar reasoning may be employed to explain the action at the anode. Therefore, in electrolysis all of the ions participate in conducting the current and collect around the electrodes, but since the $H^{\cdot}$ and OH' ions separate more easily, these are discharged. With stronger currents it is possible to cause the separation of the $K^{\cdot}$ and SO_4'' ions also, since the number of $H^{\cdot}$ and OH' ions present is too small to carry all of the current, and the energy required to discharge the ions of the electrolyte is less than that necessary to remove the small number of residual $H^{\cdot}$ and OH' ions. The formation and decomposition of water are reversible processes, so that no loss of energy is involved, as would be the case if secondary actions occurred.

Electrolytic Separation of the Metals. Freudenberg * was the first to recognize the possibility of effecting the quantitative separation of different metals by means of graded electromotive forces. He showed that it was only necessary to select a salt of each metal the decomposition potentials of which differ as widely as possible, and electrolyze at an electromotive force intermediate between these potentials. The salt having the lower decomposition potential will decompose first, and when the deposition of the metal is complete, the current will practically cease; then if the applied electromotive force be raised above the decomposition potential of the second salt, the second metal will be deposited. In practice it is found necessary to increase the applied electromotive force slightly because of the gradual decrease in the number of ions of the salt having the lower decomposition potential. The amount of this increase may be readily calculated from the familiar equation

---

* Zeit. phys. Chem., **12**, 97 (1893).

$$\pi = \frac{RT}{nF} \log_e \frac{P}{p}.$$

Suppose a mixture of the nitrates of cadmium, lead and silver is subjected to electrolysis, the decomposition potentials of the salts being as follows: — $Cd(NO_3)_2$ = 1.98 volts, $Pb(NO_3)_2$ = 1.52 volts, and $AgNO_3$ = 0.70 volt. The applied electromotive force is made a little less than 1 volt and all of the silver is deposited; then the electromotive force is raised to about 1.6 volts, thus depositing all of the lead; and finally, with an electromotive force of about 2 volts the cadmium is deposited.

In the subjoined table are given the separation potentials of some of the ions, the separation potential of the $H^{\cdot}$ ion being assumed to be equal to zero.

SEPARATION VALUES OF IONS FOR MOLAR CONCENTRATION.

Ion.	Separation Potential.	Ion.	Separation Potential.
$Ag^{\cdot}$	−0.78	I'	0.52
$Cu^{\cdot\cdot}$	−0.34	Br'	0.94
$H^{\cdot}$	0.0	O''	1.08 (in acid)
$Pb^{\cdot\cdot}$	0.17	Cl'	1.31
$Cd^{\cdot\cdot}$	0.38	OH'	1.68 (in acid)
$Zn^{\cdot\cdot}$	0.74	OH'	0.88 (in base)
		SO_4''	1.9

According to this table the decomposition potential of water is equal to the sum of the separation potentials of its ions, or 1.68 volts.

CHAPTER XXII.

PHOTOCHEMISTRY.

Radiant Energy. The visible portion of the spectrum is comprised between the extreme red at one end and the extreme violet at the other; the wave-length corresponding to the former is approximately 0.7 micron, while that corresponding to the latter is about 0.4 micron. The visible portion of the spectrum, however, is but a small fraction of the entire spectrum. Beyond the red of the visible spectrum lies the region of the so-called infra-red, comprising all wave-lengths from 0.76 micron up to 300 microns. Beyond the infra-red, between 300 and 2000 microns, is an unmeasured region, which is succeeded by the region of electrical waves, extending from 2000 microns to an undetermined maximum. On the other hand, extending beyond the violet of the visible spectrum is the so-called ultra-violet or actinic region, comprising all wave-lengths, between 0.4 micron and 0.1 micron. It thus appears that heat, light, and electricity are all forms of radiant energy, the only distinction between them being a difference in wave-length. Very little is known concerning radiant energy, and up to the present time all attempts to resolve it into a capacity and an intensity factor have failed. Whatever may be the nature of this form of energy, we know that the effects produced by it are dependent upon the wave-length of the radiation.

We have already devoted several chapters to the consideration of thermochemistry and electrochemistry, and it now remains to study very briefly the connection between chemical energy and that subdivision of radiant energy called light. This branch of theoretical chemistry is termed *photochemistry*. The ultra-violet or actinic rays are the most active chemically, although light of every wave-length, including the invisible infra-red, is capable of producing chemical action. When light falls upon a substance, a portion of the incident radiation is reflected, a portion is absorbed, and a portion is transmitted. It has been shown that only that portion of the incident radiation which is absorbed is effective in producing chemical change.

Radiant energy has been shown by Lebedew,* and also by Nichols and Hull,† to exert a definite, though extremely small pressure. Thus, the pressure of solar radiations on the earth is equivalent to that of a column of mercury 1.4×10^{-9} mm. high.

Source of Radiant Energy. According to the electromagnetic theory of light, the emission of waves of light from a material source is due to the vibrations of minute charged particles called *radiators*. These radiators, which may be either atoms or electrons, give rise to electromagnetic waves of the same period as their own, that is, to light waves of definite length. The energy required to produce these electromagnetic waves is derived from the vibrating system itself, and unless an equivalent amount of energy is constantly supplied to the system, the amplitude of the vibrations will steadily diminish and ultimately cease.

There are two different ways in which this supply of energy can be maintained. First, the temperature of the vibrating system as a whole may be kept high. This type of radiation, which is maintained by purely physical means, is called *pure temperature radiation*. Every substance whose temperature is above the absolute zero (−273°) gives rise to pure temperature radiation. The higher the temperature, the more rapid and the more energetic the atomic and electronic vibrations become. With increase in rapidity of vibration, there results a corresponding diminution in wave-length, so that, as the temperature is raised, the longer heat waves are succeeded by the shorter waves of the visible region of the spectrum. When a sufficiently high temperature is reached, the period of vibration becomes so rapid as to cause the radiation of waves corresponding to the entire range of the visible spectrum. At higher temperatures, the rate of vibration is such that the vibrating particles must of necessity possess extremely small mass: it is commonly believed that under these conditions the vibration is wholly electronic.

The second way in which energy may be supplied to the vibrating atoms or electrons is by chemical or electrical means. The general term *luminescence* has been proposed by Wiedemann for all cases where luminous energy is derived from other sources than high temperature. It is to be observed that luminescence is frequently exhibited by systems whose temperatures are comparatively low. For example, notwithstanding the fact that the flame resulting from the combustion of carbon disulphide has a temperature of only 150°, it has been found to be capable of affecting the photographic plate. Pure temperature radiation alone at 150° would correspond to long waves in the infra-red region of the spectrum and, as is well known, such waves are incapable of exerting appreciable photographic action.

---

* Rapp. pres au Congres de Physique, **2**, 133 (1900).

† Phys. Rev., **13**, 293 (1901).

Emission and Absorption. The relation between the emissive and absorptive powers of different bodies was first clearly enunciated by Kirchhoff * in 1859. This law may be stated as follows: — *Light of any given wave-length emitted by a body can also be absorbed by the same body at a lower temperature.* This law, it will be seen, offers a satisfactory explanation of the Fraunhofer lines in the solar spectrum. The sun is surrounded by a gaseous atmosphere resulting from the vaporization of the elements present in the body of the sun. Each element in the cooler gaseous envelope, according to Kirchhoff's law, absorbs those wave-lengths which it emits at the higher temperature of the solar nucleus. The resulting dark lines of the solar spectrum have enabled the astronomer to determine the elementary composition of the sun.

If the emissive and absorptive powers of a body be denoted by E and A respectively, then according to Kirchhoff's law,

$$E/A = S,$$

where S is a constant. When absorption is complete, A is unity and $S = E$. Under these conditions the constant, S, may be defined as the emissivity of a body which absorbs all of the incident radiation and reflects none. Such a body was called by Kirchhoff a perfectly *black body*. The emissivity of a perfectly black body is equal to the ratio of the emissive to the absorptive power of any body at the same temperature. A familiar qualitative illustration of Kirchhoff's law is that afforded by the appearance of a fragment of white chinaware possessing a dark pattern when heated to a high temperature. The dark parts of the design absorb light, while the white parts reflect it. On heating the fragment to redness, the pattern will be reversed, the dark portions of the design appearing bright and the white portions dark.

---

* Ostwald's Klassiker, No. 100 (1898).

It has been shown that the law of Kirchhoff is a necessary consequence of the application of the second law of thermodynamics to the thermal equilibrium within an enclosure whose walls are impervious to heat.

The Stefan-Boltzmann Law. From a study of the experiments of Dulong and Petit on the rate of cooling of different bodies, Stefan * discovered an empirical relation between the total radiation of a body and its temperature. Later, Boltzmann † derived the same relation thermodynamically and showed that instead of being general, as Stefan supposed, it is only strictly applicable to a perfectly black body. The Stefan-Boltzmann law may be stated as follows: — *The total radiation from a perfectly black body is directly proportional to the fourth power of the absolute temperature.* If the total radiation be denoted by S, we may write

$$S = CT^4,$$

where C is a constant. If the radiation from the sun be considered solely as a temperature effect, its temperature may be calculated by the above equation expressing the Stefan-Boltzmann law. Employing available bolometric data, the temperature of the sun may thus be shown to be 6200° absolute.

The Displacement Law of Wien. Having considered the total energy radiated by a given source, we now come to the consideration of the distribution of energy throughout the entire spectrum in its relation to temperature. The results of the experiments of Lummer and Pringsheim ‡ on the distribution of energy in the normal spectrum of a black body are shown by the curves of Fig. 109. The values of the energy radiated by the source are plotted as ordinates against the corresponding values of the wave-length as abscissæ. It will be observed that the energy corresponding to a definite wave-length increases with the temperature, and that each curve, or isothermal, exhibits a distinct maximum. The

---

* Sitz. Ber. Wiener Akad., **79** (II), 391 (1879).

† Wied. Ann., **22**, 291 (1884).

‡ Verh. deutsch. phys. Ges., **1**, 230 (1889); **3**, 36 (1901).

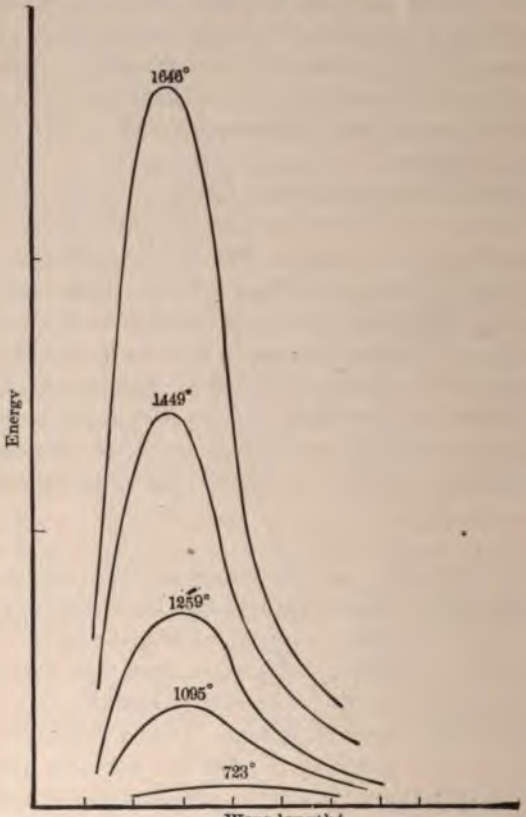


Fig. 109.

position of this maximum is displaced in the direction of decreasing wave-length as the temperature is raised.

In 1893, Wien * discovered the law governing this displacement of the energy maximum with temperature. If $\lambda_{max.}$ denotes the

---

* Wied. Ann., 58, 662 (1896).

wave-length corresponding to the energy maximum, and T is the absolute temperature of the radiating black body, Wien showed that

$$\lambda_{\text{max.}} \times T = \text{constant}.$$

Furthermore, Wien found that

$$S_{\text{max.}} = BT^5,$$

where $S_{\text{max.}}$ is the maximum emissivity corresponding to $\lambda_{\text{max.}}$. In general, the emissivity S is the amount of energy radiated per second from a narrow strip of the spectrum corresponding to the mean wave-length λ. It should be mentioned that while the experimental realization of a perfectly black body is impossible, a very close approximation can be obtained by the employment of a hollow blackened sphere perforated by a small hole to permit the passage of the radiation. When this sphere is heated, practically all of the radiation is absorbed by multiple reflections at the inner surface. It has been found that where such a black body is not available, or where extreme accuracy is not required, a thin strip of platinum foil coated with ferric oxide and heated electrically proves a satisfactory substitute. It is hardly necessary to call attention to the fact that the term black body, as here used, does not imply a total absence of color. At high temperatures, a "black" source of radiation may be red or even white. To avoid confusion, it has been proposed to substitute the term *full radiator* for the older term, black body.

Distribution of Energy throughout the Spectrum. The experimental determination of the radiant energy corresponding to a given wave-length, really resolves itself into the measurement of the energy emitted between two contiguous wave-lengths, λ and $\lambda + d\lambda$. In other words, we actually measure the energy of a very small portion of the spectrum included between two wave-lengths which lie very close together.

Several different formulæ have been proposed for the calculation of the distribution of energy throughout the spectrum. Of these, the formulæ of Rayleigh and Wien have been found to reproduce experimental values with considerable accuracy. The formula of Rayleigh has the following form:

$$S_\lambda = \frac{CT}{\lambda^4} \cdot e^{-\frac{c}{\lambda T}},$$

while that of Wien may be written thus:

$$S_\lambda = \frac{C}{\lambda^5} \cdot e^{\frac{c'}{\lambda T}}.$$

In these two formulas, C and c' are constants, while the other symbols have their usual significance. The formula of Rayleigh has been found to hold better in the region of the longer wave-lengths while the reverse is true of the formula of Wien. It should be remembered that both of these formulas apply only to bodies emitting continuous spectra.

High Temperature Thermometry.* Various optical methods for the measurement of high temperatures have been developed, but a detailed treatment of these methods is obviously out of place in a book of this character. Mention should be made, however, of two instruments which have proven of great value in high temperature measurements.

The optical pyrometer of Féry is based upon Stefan's law of total radiation. It consists of a telescope fitted with an objective of fluorite, at the focus of which is placed a sensitive thermocouple. In order to determine the temperature of a source of radiant energy, such as a crucible of molten metal, the telescope is directed toward the contents of the crucible and the image is focussed on the thermo-junction by means of an adjustable eye-piece. The resulting electric current is then measured by means of a galvanometer.

In the optical pyrometer of Holborn and Kurlbaum, use is made of the luminous radiations only. In this instrument the current through a small incandescent lamp is varied until its light is just eclipsed by that from the hot body. When this point of balance has been reached, the incandescent filament and the hot body have the same temperature. The pyrometer is calibrated by determining the current necessary to raise the filament of the lamp to the temperature of the standard black body, the temperature of the latter being determined by means of a thermocouple. Of course, when the instrument is used to determine the temperature of sources of radiant energy which differ widely in character from that of a perfectly black body, the accuracy of the measurements is lessened, but even in an extreme case, such as that presented by polished platinum at 950°, the error does not exceed 74°. The importance of optical pyrometers in photochemical investigations lies chiefly in the determination of energy curves of light sources and in the absolute measurement of radiant energy.

---

* For a detailed account of optical pyrometers, the student is referred to "High Temperature Measurements" by Le Chatelier and Boudouard, translated by Burgess (John Wiley and Sons, Inc.).

Luminescence. As has already been pointed out, it is customary to distinguish between pure temperature radiation and luminescence. The latter term is applied to all cases where chemical or electrical energy is transformed directly into radiant energy. The various types of luminescence may be conveniently classified in the following manner: —

Type of Luminescence.	*Origin of Radiation.*
(1) Photo-luminescence (*a*) Fluorescence, (*b*) Phosphorescence.	Preliminary exposure of the luminous substance to some external source of radiant energy.
(2) Thermo-luminescence.	Stimulation by heat, but at a temperature considerably lower than that required for pure temperature radiation.
(3) Chemi-luminescence.	Chemical reaction.
(4) Tribo-luminescence.	Fracture or cleavage of crystals.
(5) Cathodo-luminescence	Electric discharge.
(6) Radio-luminescence.	Radioactivity.

By the term *fluorescence* is meant the phenomenon of the emission, by an illuminated medium, of light of a different wave-length from that of the incident radiation. In general, the wave-length of the transformed radiation is greater than that of the incident radiation. This law, to which several exceptions have been discovered, was first enunciated by Stokes. When the incident radiation is cut off, fluorescence ceases.

On the other hand, there are many substances which continue to emit light for some time after the external light-stimulus is removed. This phenomenon is termed *phosphorescence* and appears to be governed by Stokes law for fluorescence. The property of phosphorescence appears to be limited to anhydrous substances.

Among the numerous substances which are known to exhibit the phenomenon of fluorescence may be mentioned fluorite (from which the phenomenon derived its name), uranium glass, petroleum, solutions of organic dyestuffs, and quinine sulphate. The vapors of sodium, mercury, and iodine have recently been found by Wood to fluoresce brilliantly.

The sulphides of the alkaline earths may be mentioned as examples of phosphorescent substances. The investigations of Lenard and Urbain have revealed the interesting fact that the presence of a trace of one of the heavy metals greatly intensifies the light emitted by a phosphorescent substance.

The phenomenon of *thermo-luminescence* calls for little comment. There seems to be an intimate connection between thermo-luminescence and phosphorescence, since the substances exhibiting the former phenomenon must be exposed initially to light, otherwise they do not emit any visible radiation on gentle heating.

Chemi-luminescence is a phenomenon accompanying many chemical reactions. Thus, the precipitation of sodium chloride from its saturated solution by hydrochloric acid gas is accompanied by an emission of light which may readily be seen if the reaction is carried out in a dark room.

When certain crystals, such as those of cane sugar, are either crushed or simply rubbed together, flashes of light are emitted. This phenomenon is known as *tribo-luminescence.*

Cathodo- and *radio-luminescence* may be considered as subdivisions of the more inclusive term, *electro-luminescence.* Attention has already been called to the fact that the residual gas in a vacuum tube is rendered luminous by the passage of the electric discharge, and also that certain minerals become phosphorescent when placed in the path of the cathode rays. These may be taken as examples of cathodo-luminescence. The luminosity of a screen coated with crystals of zinc sulphide, when subjected to the action of the α-particles shot out from a radio-active substance, has also been mentioned in a previous chapter. This is clearly an instance of radio-luminescence.

Having briefly reviewed the different processes involved in the production of light we now turn to a consideration of the chemical phenomena resulting from exposure to light.

Photochemical Action. The development of the green color of plants under the influence of the rays of the sun, and the reverse process of bleaching in darkness, were probably the first photochemical reactions to be observed. To-day it is known that light has the power of initiating or accelerating every variety of chemical change. This statement may be illustrated by the following typical photochemical reactions: — The polymerization of anthracene, the depolymerization of ozone, the transformation of maleïnoid into fumaroid forms, the hydrolysis of acetone, the oxidation of lead sulphide, and the reduction of silver salts. That such a variety of photochemical reactions should result from exposure to mixed, or heterogeneous, light is due to the selective absorption of each particular chemical system.

Photochemical action is not limited to the waves of the visible spectrum alone, but extends from the red end of the spectrum (wave-length 800 $\mu\mu$) * into the ultra-violet region (wave-length 300 $\mu\mu$). In fact, the shorter wave-lengths of the ultra-violet region of the spectrum have been found to be the most active photochemically.

Laws of Grotthuss. The two fundamental generalizations of photochemistry were first enunciated by Grotthuss in 1818. These generalizations may be stated as follows: —

(1) *Only those rays of light which are absorbed produce chemical action.*

(2) *The action of a ray of light is analogous to that of a voltaic cell.*

It has recently been shown by Bancroft † that the second of these two laws is inadequate to account for all of the known facts and, therefore, he proposes the following modification: — *All of the radiations which are absorbed by a substance tend to eliminate that substance. It is merely a question of chemistry whether any reaction occurs and what the products of the reaction will be.*

---

* 1 $\mu\mu^{-7} = 10^{-7}$ cm.

† Jour. Phys. Chem., **12**, 209, 318, 417 (1908); **13**, 1, 181, 269, 449, 538 (1909); **14**, 292 (1910).

Quantitative Relations Concerning the Absorption of Light. When a ray of light enters an absorbing medium only a certain proportion of the incident radiation is absorbed. The intensity of the light entering an absorbing medium is not equal to that which is incident on the surface of the medium, owing to the fact that a portion of the incident beam is reflected. It has been found that if the thickness of the medium be increased in arithmetical progression, the intensity of the transmitted light decreases in geometrical progression. If the intensity of the light traversing a layer dl be denoted by I, then

$$-\,dI/dl = kI, \tag{1}$$

where k is a constant depending upon the nature of the absorbing medium and the wave-length of the light. This constant k is known as the *absorption index*. If the initial intensity of the light is I_0 and the total thickness of the medium is d, equation (1) becomes, on integrating,

$$I = I_0 \cdot e^{-kd}. \tag{2}$$

Or equation (2) may be written in the form,

$$k = \frac{1}{d}\log_e \frac{I}{I_0}. \tag{3}$$

If we replace e^{-k} by α, then equation (2) becomes

$$I/I_0 = \alpha^d. \tag{4}$$

The constant α is called the *transparency* or the *transmission coefficient*. Bunsen and Roscoe introduced the term *extinction coefficient*. This quantity may be defined as the reciprocal of that thickness of the medium which reduces the intensity of the transmitted light to one-tenth of its initial value. If the extinction coefficient be denoted by ϵ, its value may be calculated from equation (2) in the following manner: —

$$I = I_0 \cdot 10^{-\epsilon d}, \tag{5}$$

or

$$\epsilon = \frac{1}{d}\log_e \frac{I}{I_0}. \tag{6}$$

It is evident that e^{-k} is identical with $10^{-\epsilon}$ or $\epsilon = mk$, where m represents the modulus of the Naperian system of logarithms.

In 1852 Beer * enunciated an important law concerning the influence of concentration on absorption. Beer's law may be stated as follows: — *The absorption of light by different concentrations of the same solute dissolved in the same solvent is an exponential function of the concentration, provided the thickness of the absorbing medium be maintained constant.* It follows from this law that

$$I = I_0\alpha^{cd}, \tag{7}$$

where c is the concentration of the solution.

If Beer's law is valid, the ratio, $c/\epsilon = A$, known as the *absorption ratio*, should be constant. Beer's law has been tested with a large number of solutions and has been found to hold quite generally where no change in the solute occurs when the concentration of the solution is altered.

Photochemical Extinction. According to the first law of Grotthuss, only the absorbed light is chemically active. The converse of this law, viz., that every substance which absorbs light undergoes chemical change, apparently does not hold. Furthermore, only a portion of the rays absorbed by a light-sensitive substance are directly involved in effecting chemical change. For example, while an alkaline copper tartrate solution shows marked absorption in the infra-red, red, yellow, and ultra-violet, it has been proven that the photochemical reduction of the copper salt to cuprous oxide is due to the action of the ultra-violet rays alone.

The first quantitative measurements of the absorption of light by a reacting system were made by Bunsen and Roscoe.† These investigators found that the absorption of light by hydrogen and chlorine, taken separately, was less than that of the reacting mixture of the two gases. From this result they concluded that in a photochemical reaction, the absorption of light by the reacting system is greater than the sum of the individual absorptions of the reacting substances. The absorption of light by the reacting system, over and above the ordinary or "optical" absorption of the reacting substances, they called *photochemical extinction*. While the phenomenon of photochemical extinction is regarded by many physical chemists as having doubtful significance, nevertheless the distinction between purely optical absorption on the one hand, and chemical absorption on the other, is quite generally accepted.*

---

* Pogg. Ann., **86**, 78 (1852).

† Ostwald's Klassiker, No. **38**.

If the distinction drawn by Bunsen and Roscoe between optical and chemical absorption be accepted, then all photochemical reactions may be regarded as belonging to one or the other of two classes, as follows: — (1) reactions in which light does work against chemical affinity, the work being equivalent to the photochemical extinction; or (2) reactions in which the light functions merely as a catalyst. In reactions belonging to the first class, the light is considered to be the agent which actually initiates chemical change, whereas in reactions of the second class, the light is assumed to accelerate reactions which would otherwise proceed at a slower rate.

Kinetics of Photochemical Reactions. Let A and B represent two chemically distinct substances, and let us assume that the reaction

$$A \rightarrow B$$

takes place under the influence of light. The course of the reaction can be followed in the usual manner by determining the amount of either constituent which is present at any definite time. There are certain factors, however, which render such kinetic measurements more difficult in the case of a photochemical reaction than in that of an ordinary chemical reaction. Let us assume that the above reaction is homogeneous and of the first order and also that it takes place in homogeneous solution. It is apparent that if the system is illuminated from one side, as shown in Fig. 110, the rate at which A undergoes transformation into B will depend upon the thick-

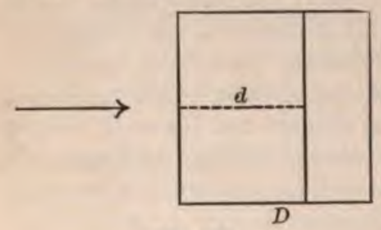


Fig. 110.

---

* For a condensed summary of the different theories of light-absorption, the student should consult Sheppard's "Photochemistry" (Longmans, Green & Co.).

ness, d, of the absorbing layer. Hence, if the velocity of the transformation be denoted by dB/dt, we may write

$$dB/dt = k[A],$$

in which the value of the constant k will not only be a function of the intensity and wave-length of the light but also of position. Furthermore, the variation in the velocity of the reaction in successive layers will cause differences in concentration which will tend to become equalized by the process of diffusion. From this example it is obvious that the extent to which light is absorbed is dependent upon the dimensions of the absorbing system.

If light be regarded as a material substance, then we may conveniently consider its absorption as analogous to the diffusion of a gas into a liquid and the light intensity at any point as the analogue of concentration or active mass. According to the law of mass action, the velocity of a chemical reaction is expressed by the equation,

$$dx/dt = kc_1^{n_1} \cdot c_2^{n_2} \ldots - k'c_1'^{n_1'} \cdot c_2^{n_2'} \ldots$$

where c_1, c_2, etc., are the concentrations of the substances entering into the reaction, and n_1, n_2, etc., are the coefficients derived from the chemical equation and indicating the order of the reaction. In applying this equation to photochemical reactions, the following possibilities must be borne in mind: —

(1) The reaction may take place in successive stages. Under these conditions the experimentally measured velocity will correspond to that of the slowest reaction.

(2) Side reactions may occur with the formation of products quite different from those resulting from the main reaction.

(3) There may be catalysis. In fact, this phenomenon is frequently met with in the study of photochemical reactions.

Nernst has pointed out that the velocity constants, k and k', in the foregoing equation, may be conveniently considered as being directly proportional to the intensity of the light, for light of the same kind. Owing to absorption, this intensity will be a function of position in the absorbing medium.

In applying the law of mass action to photochemical reactions, it is important to note that, as a general rule, the exponents n_1, n_2, etc., in the equation of the so-called *dark-reaction* are not identical with the exponents ν_1, ν_2, etc., of the *light-reaction*. In other words, the order of a chemical reaction is usually different in the light from what it is in the dark. The photochemical exponents ν_1, ν_2, etc., are never greater than, and are seldom equal to, the corresponding exponents n_1, n_2, etc., of the dark-reaction.

Thus, Bodenstein[*] showed that the dissociation of hydriodic acid, in the dark, is a reaction of the second order and may be represented by the equation

$$2\,HI \rightleftarrows H_2 + I_2,$$

whereas when hydriodic acid dissociates in the light, the reaction is of the first order, as shown by the equation

$$HI \rightleftarrows H + I.$$

In this case, the light acts as a catalyst, merely accelerating the velocity of the dark-reaction.

The action of light on the reverse reaction may be such as to oppose its usual course in the dark. In this case the resulting photochemical equilibrium, or so-called *photo-stationary state*, will not be identical with the corresponding chemical equilibrium. It should be observed that the photo-stationary state differs from ordinary chemical equilibrium, in that its permanency is wholly dependent upon the constancy of the source of illumination; *i.e.*, when the light is cut off, the photo-stationary state shifts to the ordinary chemical equilibrium, provided the reaction is reversible. It has also been found that the temperature coefficients of most photochemical reactions are negligible.

Becquerel[†] discovered that silver chloride, which had been precipitated in the dark, was only sensitive to short wave-lengths of light, whereas silver chloride, which had been exposed for a few moments to sunlight, became sensitive to all wave-lengths in the visible spectrum and to the shorter wave-lengths of the infra-red. This phenomenon, which has been observed with various substances, was first studied systematically by Bunsen and Roscoe[‡] who termed it *photochemical induction*.

---

[*] Zeit. phys. Chem., **22**, 23 (1897).

[†] Ann. Chim. Phys. [3], **9**, 257 (1843).

[‡] Pogg. Ann., **100**, 481 (1857).

Employing a mixture of hydrogen and chlorine gases they found that under constant illumination, the velocity of formation of hydrochloric acid, which was hardly appreciable at first, increased rapidly to a maximum and then remained constant. The interval of time required for the reaction to attain its maximum velocity is known as the *period of induction*.

It has been found that in almost every photochemical reaction there is a similar period of initial perturbation. The phenomenon has been thoroughly investigated by Burgess and Chapman[*] who arrived at the conclusion that induction effects are to be ascribed to the presence of minute traces of various impurities, such as gases or water vapor, adsorbed by the walls of the reaction-vessel. We may therefore conclude that induction effects are not characteristic of photochemical reactions.

Classification of Photochemical Reactions. According to Sheppard ("Photochemistry") photochemical reactions may be conveniently classified in the following manner: —

(1) Reversible reactions, *i.e.*, reactions in which the products formed under the influence of light react to reproduce the original system when the light is removed.

(2) Irreversible reactions, *i.e.*, reactions in which the light promotes transformation to a more stable system. Irreversible reactions are subdivided into —

(a) Complete reactions; and
(b) Pseudo-reversible reactions.

The polymerization of anthracene may be taken as an example of a reversible photochemical reaction. This reaction may be represented as taking place according to the equation

$$2\,C_{14}H_{10} \underset{\text{dark}}{\overset{\text{light}}{\rightleftarrows}} C_{28}H_{20},$$

the upper arrow indicating the direction of the light-reaction (polymerization) and the lower arrow that of the dark-reaction (depolymerization).

An illustration of a completely irreversible photochemical reaction is afforded by a mixture of hydrogen and chlorine gases which combine, on exposure to light, to form hydrochloric acid gas, according to the equation

---

[*] Jour. Chem. Soc., **89**, 1402 (1906).

$$H_2 + Cl_2 \xrightarrow{\text{light}} 2\,HCl.$$

If the hydrochloric acid is removed by solution in water as fast as it is formed, the velocity of the reaction will be directly proportional to the intensity of the light. Bunsen and Roscoe * made use of the foregoing facts in the construction of their actinometer.

The reduction of ferric oxalate may be taken as an example of a pseudo-reversible photochemical reaction. This substance is reduced to ferrous oxalate on exposure to light as shown by the equation

$$Fe_2(C_2O_4)_3 \xrightarrow{\text{light}} 2\,Fe\,(C_2O_4) + CO_2.$$

In the dark, ferrous oxalate is re-oxidized to ferric oxalate by the oxygen of the air. While the initial substance is reproduced, it is evident that the reaction is not strictly reversible.

Actinometers. A number of different forms of apparatus have been devised for measuring the chemical action of light: such instruments are known as *actinometers.*

The hydrogen-chlorine actinometer is based upon the well-known fact that the speed of the reaction between hydrogen and chlorine varies greatly with the intensity of illumination. Bunsen and Roscoe,† guided by the experiments of Draper, constructed an actinometer in which the rate of combination of hydrogen and chlorine could be measured by allowing the hydrochloric acid formed to dissolve in water, and noting the resulting diminution of volume. A diagram of this apparatus is given in Fig. 111. The apparatus is filled with a mixture of equal parts of hydrogen and chlorine, obtained by the electrolysis of a solution of hydrochloric acid. The bulb *A*, containing water, is connected at one end with a tube fitted with a stop-cock *B*, and at the other end with a horizontal tube terminating in a reservoir *D*, which also contains water. When the water has become saturated with the constituents of the gaseous mixture, *B* is closed and the entire apparatus is protected from light. When it is desired to measure the photochemical action of a source of light, the bulb *A* is uncovered and the light is allowed to fall upon it. Some of the hydrogen and chlorine will combine, and the hydrochloric acid formed will be absorbed by the water in *A*; the column of water in the horizontal tube will move to the right, the magnitude of the movement being measured on the scale *C*. In this way the amount of photochemical action can be determined. An objection to the use of hydrogen and chlorine in the actinometer is the danger of violent explosions when the illumination is too intense. To remove this objection, Burnett replaced the hydrogen of the mixture by carbon monoxide.

---

* "Photochemische Untersuchungen," Ostwald's Klassiker, No. 34.

† Pogg. Ann., **100,** 43 (1857); **101,** 235 (1857).

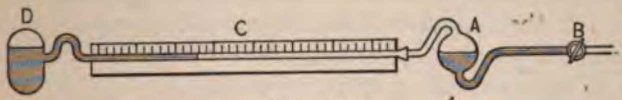


Fig. 111.

Action of Light on the Silver Halides. Probably the most familiar, and undoubtedly one of the most important, photochemical reactions is that which takes place on the exposure of a photographic plate.* Luther † has shown that when a pure silver halide is exposed to light, it undergoes reduction according to the equation

$$2\,AgX \xrightarrow{\text{light}} Ag_2X + X,$$

where X may be chlorine, bromine, or iodine. On removing the light, the sub-halide recombines with the free halogen as shown by the equation

$$Ag_2X + X \xrightarrow{\text{dark}} 2\,AgX.$$

In other words, the reaction is strictly reversible and a well-defined photo-stationary state results from a given intensity of illumination. The investigations of Baker * make it appear quite probable that the photochemical reduction of the silver halides is dependent upon the presence of a minute trace of water vapor as a catalyst.

---

* For an excellent treatment of the chemistry of photography the student is recommended to consult "Photography for Students of Physics and Chemistry," by Louis Derr (Macmillan); or "Photochemie und Beschreibung der photographischen Chemikalien," by H. W. Vogel.

† Zeit. phys. Chem., **30**, 628 (1899).

In the photographic plate, the silver halide is embedded in gelatine, which not only accelerates the rate of reduction of the silver halide but also causes the reaction to become irreversible. The alteration in the behavior of the silver halide, brought about by the presence of gelatine, is due to the fact that the latter reacts with the free halogen according to the equation

$$2\,AgBr + \text{gelatine} \xrightarrow{\text{light}} Ag_2Br + \text{brominated gelatine.}$$

The continuous removal of the liberated bromine by the gelatine is an example of what is known as *photochemical sensitization.* Another example of photochemical sensitization is afforded by a mixture of benzene and silver chloride. The normal darkening of the silver salt is markedly increased by the presence of the benzene, which combines with the chlorine as rapidly as it is set free by the action of the light on the silver halide.

While the silver bromide of the photographic plate is extremely sensitive to the shorter wave-lengths corresponding to the violet and ultra-violet regions of the spectrum, it is only reduced by the longer wave-lengths after prolonged exposure. It has been found, however, that the addition of certain dyestuffs, such as eosine and Congo-red, renders the silver halide sensitive to the longer wave-lengths of the spectrum. This phenomenon, which is known as *optical sensitization,* must be carefully distinguished from chemical sensitization to which reference has already been made. It is to be noted that an optical sensitizer does not absorb chemically any of the products of the reaction. Photographic plates which have been sensitized in this way are commonly known as ortho-chromatic plates.

All of the dyestuffs which can function as optical sensitizers have been found to exhibit anomalous refraction; *i.e.,* for wave-lengths slightly longer than those absorbed, these substances possess an abnormally large refractive index, in consequence of which the refracted waves exert the same effect upon the silver halide as the shorter wave-lengths of the spectrum. Although it is not an essential property, it is generally found that optical sensitizers are fluorescent.

---

* Jour. Chem. Soc., **61,** 782 (1892).

As an example of optical sensitization, where the sensitizer is non-fluorescent, we may take the photochemical reduction of mercuric chloride in the presence of ammonium oxalate. This reaction takes place according to the equation

$$2\,HgCl_2 + (NH_4)_2C_2O_4 \xrightarrow{\text{light}} Hg_2Cl_2 + NH_4Cl + 2\,CO_2.$$

The presence of the non-fluorescent ferric ion, $Fe^{\cdot\cdot\cdot}$, has been shown by Winther * to be an effective optical sensitizer in the reaction. The ferric ion is reduced to the ferrous state while the oxalic acid undergoes oxidation by the mercuric chloride. It was pointed out by Eder † that this reaction is well adapted for actinometric measurements, since the amount of mercurous chloride precipitated is directly proportional to the intensity of the light.

Photochemical After-Effect. Certain photochemical reactions have been discovered in which the reaction proceeds even after the light stimulus is removed. This phenomenon is known as the *photochemical after-effect.* The velocity of a reaction of this kind is different from that of either the light- or the dark-reaction. It has also been found that if a portion of the reaction-mixture, which has already been exposed to the light, be added to a fresh unexposed portion, the latter immediately commences to decompose. Thus, a solution of iodoform in chloroform becomes brown, on exposure to light, due to liberation of iodine.

If the solution is removed from the light, the decomposition will continue for several days, and if a small portion of the partially decomposed solution be added to a freshly prepared solution, the latter will commence to decompose. The photochemical after-effect can be readily explained if we assume that the action of light gives rise to heterogeneous nuclei which persist for a sufficient time after the light is removed to act as centers around which the reaction can proceed throughout the unexposed portion of the mixture.

---

* Zeit. wiss. Phot., 7, 409 (1909).

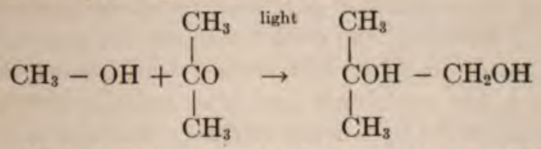
† Sitz. ber. Wien. Akad. (1879).

Assimilation of Carbon Dioxide. A photochemical reaction of special interest to the biologist is that in which atmospheric carbon dioxide is taken up by plants under the influence of solar radiation. While the reaction is exceedingly complex, it may be regarded as taking place according to the hypothetical equation

$$6\,CO_2 + 5\,H_2O \xrightarrow{\text{light}} \underset{\text{(starch)}}{C_6H_{10}O_5} + 6\,O_2.$$

This reaction represents a gain in energy amounting to approximately 685 calories per formula-weight of starch. It is quite probable, however, that the initial product of the reaction is formaldehyde and that subsequently the latter substance undergoes polymerization with the formation of starch and other carbohydrates. The green coloring matter of the leaves of plants, known as chlorophyll, also plays an important part in the assimilation of carbon dioxide, but beyond the fact that its action is not catalytic, little can be stated as to the manner in which it functions in the reaction. The velocity of the reaction has been found to attain its maximum value in yellow and green light, a result which is in complete agreement with the fundamental law of Grotthuss that only those rays which are absorbed are active chemically. As has already been stated, the temperature coefficients of photochemical reactions are generally very small. This is not true, however, of the reaction under consideration. It has been found that the rate at which carbon dioxide is assimilated by a plant is nearly doubled for a rise in temperature of 10° (see p. 377).

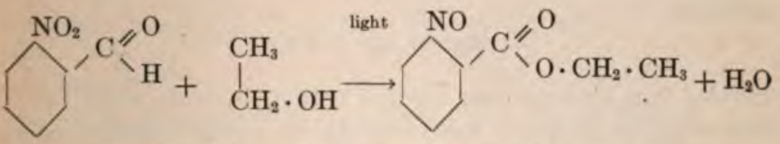
Photochemical Synthesis. While it has long been known that light is capable of effecting the synthesis of complex organic compounds in the living plant from carbon dioxide and water, it is only recently that its efficiency in bringing about a great variety of organic reactions has been fully recognized. Owing to the researches of Ciamician and others in this field, numerous photochemical syntheses of considerable practical value to the organic chemist have been discovered. It must suffice here to mention a few typical photochemical syntheses. Alcohols may be oxidized in successive steps, the action of the light closely resembling the action of ferments. Methyl alcohol and acetone react to form isobutylene glycol according to the equation



$$\begin{matrix} & \mathrm{CH_3} & & \mathrm{CH_3} & \\ & | & & | & \\ \mathrm{CH_3-OH+} & \mathrm{CO} & \xrightarrow{\text{light}} & \mathrm{COH} & \mathrm{-\,CH_2OH} \\ & | & & | & \\ & \mathrm{CH_3} & & \mathrm{CH_3} & \end{matrix}$$

The action of light has been found to be especially favorable to such processes as the foregoing, involving reciprocal oxidation and reduction.

Ortho-nitro-benzaldehyde in the presence of ethyl alcohol reacts to form the ethyl ester of o-nitroso-benzoic acid as shown by the equation



Photoelectric Cells. The absorption of light by any one of the three states of matter is invariably accompanied by a change in electrical condition. The different electric effects accompanying the absorption of radiant energy have been classified by Sheppard in the following manner: —

(1) Ionization with a corresponding increase of conductance in gases, liquids, and solids caused by transmission of light.

(2) Indirect ionization of a gas due to reflection or emission of electrons from the surface of a contiguous denser phase.

(3) Development of electromotive forces in cells of the following type: —

Electrode A (light)	Conductor, Di-electric	Electrode A (dark)

where the two electrodes are separated by a medium which is partially a conductor and partially a di-electric.

The treatment of the first and second of these three classes of photoelectric phenomena properly lies within the domain of pure physics. The third class, however, includes a number of photogalvanic combinations of considerable interest and importance to the physical chemist.

The first investigation of photoelectric combinations was undertaken by E. Becquerel [*] in 1839. He prepared a cell consisting of identical plates of pure silver, coated with a silver halide, and immersed in dilute sulphuric acid as an electrolyte. On exposing one electrode to the light, while the other was kept in the dark, an appreciable electromotive force was developed, the current flowing in the solution from the darkened to the illuminated electrode. If a galvanometer be included in the circuit, the deflection of the needle may be taken as a measure of the intensity of the light.

The action of the Becquerel actinometer has been explained by Ostwald as follows: — The incident light lessens the stability of the silver iodide, which undergoes ionization according to the equation

$$AgI \rightarrow Ag^{\cdot} + I':$$

the $Ag^{\cdot}$ ions give up their charges to the electrode while the I' ions enter the solution. For every $Ag^{\cdot}$ ion which is discharged at the illuminated electrode, an equal number of $Ag^{\cdot}$ ions enter the solution at the darkened electrode, thus charging the latter negatively. Hence the current flows in the solution from the darkened to the illuminated electrode. Rigollot [†] has constructed an electrical actinometer in which the silver plates used by Becquerel are replaced by two oxidized copper electrodes, while instead of dilute sulphuric acid a dilute solution of sodium chloride is used.

A number of photoelectric combinations have been investigated by Wildermann, [‡] among which he recommends the following as being especially suitable for actinometers: —

---

[*] Ann. Chim. Phys. [3], **9**, 257 (1843).

[†] Jour. de Phys. [3], **6**, 520 (1897).

[‡] For a thorough treatment of theoretical photochemistry, the student is referred to Sheppard's "Photochemistry," while Plotnikow's "Photochemische Versuchstechnik" is recommended as an excellent guide to practical laboratory methods.

$$\text{(a)}\ \underset{\text{(light)}}{\text{Ag}}\ |\ \text{AgBr, 0.1 N KBr}\ |\ \text{AgBr}\ |\ \underset{\text{(dark)}}{\text{Ag}}$$

$$\text{Reaction,}\quad 2\ \text{AgBr} \rightarrow \text{Ag}_2\text{Br},$$

$$\text{(b)}\ \underset{\text{(light)}}{\text{Cu}}\ |\ \text{CuO}\ |\ \text{NaOH}\ |\ \text{CuO}\ |\ \underset{\text{(dark)}}{\text{Cu}}$$

$$\text{Reaction,}\quad 2\ \text{CuO} \rightarrow \text{Cu}_2\text{O}.$$

Of these two cells, the latter is perhaps the better, since it gives an appreciable electromotive force for light of the same intensity and varying wave-length.

While all of the theoretical interpretations of the action of photoelectric cells are more or less inadequate, the investigations of Scholl and others make it appear probable that negative electrons enter the electrolyte from the electrode, while positive ions are discharged on the electrode, thereby causing anodic polarization. In general the direction of the photoelectric current inside the cell is from the non-exposed to the exposed electrode.

INDEX OF NAMES

Abegg, 218.
Alexieeff, 172, 174.
Amagat, 74, 75.
Andrews, 105.
Ångström, 141.
Arrhenius, 211, 227, 368, 377, 392, 413, 425, 428, 432.
Aston, 63, 419.
Avogadro, 9, 76.

Babo, 208.
Baker, 521.
Baly, 140, 141, 142.
Barlow, 159.
Barnes, 262.
Bassett, 395.
Bates, 430.
Beccaria, 385.
Bechhold, 259.
Beckmann, 220.
Becquerel, 42, 518, 526.
Beer, 515.
Bergmann, 312.
Berkeley, Earl of, 197, 200, 201.
Bernoulli, 76.
Berthelot, 289, 308, 313, 323, 326.
Berthollet, 4, 312.
Berzelius, 16, 386.
Bigelow, 381.
Biltz, 260, 429.
Bingham, 119.
Biot, 132.
Blagden, 217.
Blake, 253, 254.
Bodenstein, 317, 518.
Boettger, 415.
Boguski, 377.
Boltwood, 44, 56.
Boltzmann, 76, 507.
Boyle, 2, 49, 72, 76, 170, 192, 197, 286.
Bragg, W. H., 160.
Bragg, W. L., 160.
Bredig, 276, 381, 409.
Brown, 279.
Brühl, 127.
Bruni, 250.
Budde, 81.
Buff, 121.
Bunsen, 169, 170, 514, 515, 518, 520.
Burgess, 519.
Burton, 253.

Cailletet, 118.
Callendar, 201.
Carlisle, 385.
Chapman, 519.
Charpy, 353.
Ciamician, 524.
Claude, 115.
Clausius, 76, 392, 413.
Clement, 96, 382, 383.
Cotton, 252.
Crookes, 33, 47, 48.
Cumming, 472.
Curie, 43, 44, 49, 56.

Dale, 126, 152.
Dalton, 1, 7, 16, 168.
Davy, 385, 386.
Debierne, 44.
Debray, 328.

Debye, 161.
De Chancourtois, 21.
De Forcrand, 334.
Denham, 480.
Desch, 142.
Desormes, 96, 382, 383.
Deville, 88, 321.
De Vries, 201, 202, 203, 204, 230.
Dewar, 114.
Döbereiner, 21.
Draper, 520.
Drude, 151.
Duclaux, 248.
Dulong, 11, 162.
Dumas, 20.
Dutoit, 419.

Eder, 523.
Einstein, 283, 285.
Eötvös, 146.

Fanjung, 418.
Faraday, 7, 138, 150, 268, 389.
Faure, 499.
Féry, 510.
Fick, 206, 208.
Forbes, 466.
Fletcher 285.
Freudenberg, 502.
Freundlich, 254, 264, 269, 270.
Friderich, 419.
Fuchs, 493.

Gay-Lussac, 8, 76, 192, 196, 197, 208.
Geiger 40, 52, 54, 55, 57.
Geoffroy 312.
Gibbs, 273, 274, 338, 448.
Gladstone, 126, 152.
Goodwin, 468.
Gouy, 279.
Graham, 206, 237, 274, 276.
Grotthuss, 391, 513, 524.
Grove, 392.
Guldberg, 314, 329.
Guthrie, 349.

Hall, 66.
Hamburger, 204, 205.
Hampson, 114.
Hardy, 253, 256.
Harkins, 63, 66.
Hartley, 140, 142, 144, 197.
Hautefeuille, 317.
Haüy, 159.
Hedin, 205.
Helmholtz, 448, 477.
Henry, 170, 184.
Henderson, 472.
Hess, 290, 304, 305.
Heycock, 353.
Heydweiller, 414.
Hittorf, 393.
Holborn, 478, 510.
Horstmann, 331.
Hulett, 181.
Hull, 505.

Isambert, 330.

Jones, 219, 233, 395, 418.
Jurin, 144.

Kirchhoff, 506.
Knoblauch, 375.
Koelichen, 426.
Kohlrausch, 400, 413, 414, 415, 416, 417 478, 488.
Konowalow, 175, 176.
Kopp, 14, 88, 120, 121, 127.
Kraus, 430.
Kroenig, 76.
Kundt, 98.
Kurlbaum, 510.

Laborde, 56.
Landolt, 4.
Langbein, 302.
Laplace, 98, 290.
Larmor, 373.
Lavoisier, 2, 286, 290.
Lebedew, 505.

Le Bel, 134, 135, 137.
Le Blanc, 493, 495, 497, 501.
Le Chatelier, 95, 309.
Lehmann, 165.
Lemoine, 317.
Lenard, 36.
Lewis, 162, 472, 474.
Liebig, 382.
Lillie, 249.
Linde, 114.
Lindemann, 164.
Linder, 243, 251, 254.
Lippmann, 459.
Lodge, 411.
Loomis, 218.
Lorentz, 126, 152.
Lorenz, 126, 152.
Lossen, 121.
Lüdeking, 267.
Lummer, 507.
Lundén, 442.
Luther, 521.

Mac Innes, 472.
Marignac, 5, 16.
Maxwell, 76.
Mayer, 94, 290.
Mendeleeff, 22.
Menschutkin, 378.
Meyer, 466.
Meyer, Lothar, 22, 28.
Meyer, Victor, 83.
Millikan, 40, 285.
Mitscherlich, 14.
Morgan, 149, 150.
Morley, 16.
Morse, 194, 196, 197, 198, 200.
Moseley, 60.
Mouton, 252.

Natanson, 91.
Nernst, 119, 141, 151, 164, 297, 335, 336, 419, 451, 472, 475, 476, 486, 517.
Neumann, 13.
Neville, 353.
Newlands, 22.
Newton, 312.
Nicholson, 385.
Nollet, Abbé, 188.
Nordlund, 285.
Noyes, 372, 377.
Nuttall, 52.

Ohm, 388.
Olszewski, 113.
Onnes, 116.
Ostwald, W., 8, 147, 169, 191, 231, 273, 287, 368, 379, 383, 393, 422, 424, 435, 447, 526.
Ostwald, Wo., 245.

Palmaer, 453.
Pappada, 250.
Pasteur, 132, 133, 134.
Pauli, 254.
Pebal, 90.
Perkin, 138.
Perrin, 35, 250, 279, 280, 281, 282, 283, 285.
Petit, 11, 162.
Pfeffer, 188, 189, 190, 191, 192, 193, 194, 198.
Philip, 170.
Pictet, 113.
Picton, 243, 251, 254.
Planck, 40, 207, 472, 474.
Planté, 499.
Pope, 159.
Pringsheim, 507.
Proust, 5.
Prout, 20.
Pulfrich, 124.

Quincke, 250.

Ramsay, 49, 146, 147, 148, 149, 150, 168.
Raoult, 209, 210, 212, 215, 217, 218, 223.

Rayleigh, 509.
Regener, 40, 54.
Regnault, 83.
Reicher, 368.
Reinitzer, 165.
Reuss, 250.
Richards, 16, 159, 466.
Rigollot, 526.
Roberts-Austen, 185, 353, 355.
Rodewald, 267.
Roentgen, 42.
Roozeboom, 351, 353.
Roscoe, 177, 514, 515, 518, 520.
Rose, 313.
Royds, 55.
Rudolphi, 430.
Rutherford, 40, 45, 46, 48, 49, 50, 54, 55, 57.

Sargent, 472, 474.
Schiff, 121.
Scholl, 527.
Schroeder, 265.
Shields, 146, 147, 148, 149, 150.
Siedentopf, 241.
Snell, 124.
Soddy, 48, 49, 50, 51, 52, 60.
Soret, 208.
St. Gilles, Pean de, 313, 323.
Stas, 16, 20.
Stefan, 507.
Steno, 155.
Stokes, 39, 283.
Svedberg, 277.

Tammann, 206.
Thilorier, 113.
Thomsen, 302.
Thomson, J. J., 35, 45, 68, 282, 387, 419.
Thorpe, 121.
Traube, 122, 129, 188.
Trouton, 118.

Van der Stadt, 373.
Van der Waals, 31, 81, 82, 107, 121, 171.
Van't Hoff, 135, 137, 184, 185, 192, 193, 196, 197, 213, 217, 218, 223, 226, 324, 337, 378, 412, 430.
Volta, 385, 446.

Waage, 314, 329.
Walden, 404.
Walker, 117, 211, 376.
Warder, 368.
Washburn, 417.
Weber, 12, 13.
Weimarn, 245.
Wenzel, 312.
Whetham, 412.
Whitney, 253, 254, 377.
Wiedemann, 250, 267.
Wien, 508, 509.
Wiener, 279.
Wildermann, 526.
Williamson, 392.
Wilson, C. T. R., 45.
Wilson, E. D., 63.
Winther, 523.
Wladimiroff, 205.
Wood, 512.
Wroblewski, 113.
Wüllner, 208.

Young, 183.

Zsigmondy, 241, 259.

INDEX OF SUBJECTS

Abnormal solutes, 225.
Absolute index of refraction, 125.
Absorption and emission, 506.
Absorption index, 514.
Absorption of light, quantitative relation concerning, 514.
Accumulators, 488.
Actinometers, 520.
Active deposits, 49.
Activity and concentration, 478.
Adsorption, 267.
  of gases, 268.
  in solution, 269.
  isotherm, 269, 270.
Alloys, 353.
Amicrons, 239.
Association in solution, 225.
Atomic theory, 6, 7.
  number, 58.
  structure, 57.
  structure, hydrogen-helium system of, 63.
  weights, 16, 18.
  weights and atomic numbers, relation between, 64.
Autocatalysis, 381.
Avogadro constant, 40.
  hypothesis of, 9, 79.

Basicity of organic acids, 434.
Bimolecular reactions, 366.
Boiling point constant, 213.
  and critical temperature, 119.
  elevation of, 213.
  elevation and osmotic pressure, 216.
Blood corpuscle method, 204.
Brownian movement, 279.
  recent investigations of, 285.

Calorimeter, combustion, 289.
Capillary electrometer, 458.
Carbon dioxide, assimilation of, 523.
Catalysis, 379.
  mechanism of, 352.
  negative, 382.
Cataphoresis, 251.
Cathode particle, charge carried by, 38.
  ratio of charge to mass of, 38.
  velocity of, 36.
Cathode rays, 33.
  properties of, 33.
Cathodo-luminescence, 512.
Cells, electromotive force of concentration, 411.
  galvanic, 446.
  gas, 485.
  photo-electric, 525.
  reversible, 448.
  standard, 457.
  storage, 488.
Chemical constitution, 132, 142.
Chemi-luminescence, 512.
Colloidal solutions, 238.
  density of, 245.
  electrical conductance of, 253.
  osmotic pressure of, 247.
  preparation of, 274.
  surface tension of, 247.
  viscosity of, 246.
Colloids, 237.

Colloids, molecular weight of, 249.
  precipitation by electrolytes, 254.
  surface energy of, 271.
Components, 338.
Compounds, 2, 7.
Compressibilities of solid elements, 159.
Concentration and activity, 478.
  elements, 465.
Conductance, and ionization, 412.
  at high temperatures and pressures, 417.
  determination of, 400.
  equivalent, 398.
  molar, 398.
  specific, 398.
Conductance of difficultly soluble salts, 415.
  of different substances, 402.
  of fused salts, 420.
  of non-aqueous solutions, 418.
  temperature coefficient of, 416.
Conduction of electricity through gases, 31.
Connection between gaseous and liquid states, 104.
Consecutive reactions, 376.
Corresponding conditions, 110.
Co-volume, 121.
Critical pressure, 105.
  temperature, 105.
  volume, 105.
Crookes' dark space, 32.
Cryohydrate, 347.
Crystal form and chemical composition, 158.
Crystallography, 154.
Crystalloids, 237.
Crystals, liquid, 165.
  mixed, 14.
  properties of, 156.
Crystallization methods, 275.

Decomposition potential, 495.
Degree of dissociation, calculation of, 91.
Degree of dissociation, freedom, 339.
Density of colloidal solutions, 245.
Dialysis, 237.
Dielectric constants, 150.
Diffusion, coefficient of, 206.
Dilution law, 422.
Disintegration hypothesis, 50.
  series, 52.
Dispersity, 238.
Dispersoids, 239, 245.
  classification of, 244.
Dissociation constant, 320.
  hypothesis, 437.
  in solution, 226.
Distillation fractional, 178.
  steam, 179.
Distribution of a solute between two immiscible solvents, 335.
Drop weight, 149.

Electrical conductance of colloidal solutions, 253.
  double layer, 452.
Electrode, dropping, 463.
  hydrogen, 464.
  normal, 461.
  null, 463.
Electrodes, of first type, 468.
  of second type, 468.
Electroendosmosis, 250.
Electro-luminescence, 512.
Electrolytes, ionization of strong, 429.
  mixtures with a common ion, 427.
Electrolytic dissociation theory, 227, 229.
  separation of metals, 502.
Electrometer capillary, 458.
Electromotive force, measurement of, 455.
Electrons, sources of, 41.
Electron theory, 31.
Elements, 2.
  classification of, 20.
  oxidation and reduction, 482.

Elements, periodic series of, 24.
Elevation of boiling point, 213.
Emanations, 48.
Emission and absorption, 506.
Emulsions, 239.
Emulsoids, 239.
  action of heat on, 257.
  precipitation of, 257.
Energy evolved by radium, 56.
  distribution in spectrum, 509.
Equation of condition, reduced, 111.
Equation of Nernst-Lindemann, 164.
  van der Waals, 81, 107.
Equilibrium constant, 316.
  variation with temperature, 324.
Equilibrium, homogeneous, 312.
  in homogeneous gaseous systems, 317.
  in liquid systems, 322.
Equivalent, chemical, 6.
  electrochemical, 390.
Etch figures, 158.
Eutectic, 353.

Faraday dark space, 32.
Ferments, inorganic, 381.
Fluorescence, 511.
Formation, heat of, 294.
Freezing point, lowering of, 217.
  of concentrated solutions, 233.
Fusion, heat of, 153.

Galvanic cells, 446.
Gas, ideal, 75.
  perfect, 75.
Gases, adsorption of, 268.
  specific heat of, 100.
Gas constant, molecular, 73.
  specific, 73.
Gas laws, deviations from, 74.
Gaseous and liquid states, connection between, 104.
Gaseous molecule, mean velocity of translation of, 80.
Gelation, 239.
Gels, elastic, 265.
  hydration and dehydration of, 263.
  non-elastic, 264.
  physical properties of, 262.
Gold-number, 259.

Hæmatocrit method, 205.
Heat, of combustion, 302.
  of dilution, 297.
  of dissociation of solids, 334.
  of formation, 294.
  of fusion, 153.
  of imbibition, 266.
  of ionization, 397, 432.
  of neutralization, 305.
  of reaction, variation with temperature, 300.
  of solution, 295.
  of vaporization, 118.
Helium atoms and α-particles identical, 55.
Helium, rate of production of, 56.
Helix of de Chancourtois, 21.
Heterogeneous systems, 328.
Homogeneous gaseous systems, equilibrium in, 317.
Hydrogel, 328.
Hydrolysis, 437.
  determination of, 442, 480.
Hydrosol, 238.

Imbibition, 266.
  in solutions, 267.
  velocity of, 266.
Immiscibility, 178.
Inorganic ferments, 381.
Ionic product, 433.
Ionization constant, 422.
  of water, 443.
Ionization of gases, 45.
Ionization, heat of, 432, 484.
  influence of substitution on, 435.
  of water, 487.
Ionogen, 229.
Ions, 45.

Ions, absolute velocity of, 409.
  existence of free, 391.
  migration of, 393.
Isohydric solutions, 428.
Isomorphism, 14.
Isothermals, 105.
Isotopes, 63.
Isotonic coefficient, 203.

Kinetic equation, deductions from, 78.
  derivation of, 77.
  theory of gases, 100.
Kinetics, chemical, 359.

Labile solutions, 183.
Law of Beer, 141, 515.
  of Boyle, 73, 78.
  of combining proportions, 5.
  of conservation of mass, 3.
  of constant heat summation, 290.
  of definite proportions, 4.
  of Dulong and Petit, 11.
  of Faraday, 389.
  of Gay-Lussac, 73, 79.
  of Graham, 80.
  of Grotthuss, 513.
  of Guldberg and Waage, 314.
  of Henry, 170, 171.
  of Hess, 290, 305.
  of Jurin, 144.
  of Kirchhoff, 506.
  of Kohlrausch, 406.
  of Lavoisier and Laplace, 290.
  of mass action, 314.
  of Mitscherlich, 14, 15.
  of molecular displacement, 283.
  of multiple proportions, 5.
  of Neumann, 14.
  of octaves, 22.
  of Ohm, 388.
  of Raoult, 209.
  of Richter, 4.
  of Stefan-Boltzmann, 507.
  of volumes, 8.
  of Wien, 507.
Light, action on silver halides, 521.
Liquefaction of gases, 112.
Liquids, characteristics of, 104.
  refractive power of, 123.
  vapor pressure of, 117.
Liquid systems, equilibrium in, 322.
Luminescence, 511.
Lyotrope series, 239.

Magnetic rotation, 138.
Mass, conservation of, 3.
Mass action, law of, 314.
Maximum work, principle of, 308.
Mechanism of catalysis, 382.
Membranes, semi-permeable, 191.
Metastable solutions, 183.
Microns, 238.
Miscibility, complete, 174.
  partial, 172.
Mixtures, specific refraction of, 128.
Molar volume, 10.
Molecular gas constant, evaluation of, 74.
  magnetic rotation, 139.
  refraction, 126.
  rotation, 131.
  vibration, 142.
  volume, 120.
  weight, 83, 146.
  weight by boiling point method, 215.
  weight by freezing point method, 220.
  weight in solution, 222.
  weight of colloids, 249.
  weight in solution, 222.
  vibration, 142.
  volume, 120.

Neutralization, heat of, 305.
Nitrogen peroxide, dissociation of, 93.
Non-dissociating solvent, solution of solid in, 336.
Normal electrodes, 461.

Octaves, law of, 22.
Optical activity, 132.
Osmotic pressure, 187, 191.
  and boiling point elevation, 216.
  and diffusion, 206.
  and freezing point depression, 221.
Osmotic pressure and lowering of vapor pressure, 211.
  comparative values of, 201.
  measurement of, 189.
  of colloidal solutions, 247.
  recent work on direct measurement of, 194.
  theoretical value of, 192.
Oxidation and reduction elements, 482.

Particles, α-, 55.
Peptization, 276.
Periodic law, 22, 64.
  applications of, 26.
  defects in, 29.
Periodicity of physical properties, 25.
  of radio-elements, 61.
Phase rule, 338.
  derivation of, 339.
Phosphorescence, 511.
Photochemical action, 513.
  after effect, 523.
  extinction, 515.
  induction, 518.
  reaction, kinetics of, 516.
  sensitization, 522.
  synthesis, 524.
Photo-electric cells, 525.
Photo-stationary state, 518.
Physical properties of ionized solutions, 231.
Plasmolytic methods, 201.
Polarization, 492.
  capacity of electrodes, 494.
  electromotive force of, 492.
  theory of, 497.
Polarized light, rotation of plane of, 129.
Polymorphism, 158.
Potential, between metal and solution, 464.
  decomposition, 495.
  difference at junction of two solutions, 469.
  difference at liquid junctions, 472.
  normal electrode, 475.
Precipitation and valence, 256.
Precipitation of colloids by electrolytes, 254.
  of emulsoids, 257.
  of suspensoids, 254.
Preparation of colloidal solutions, 274.
Principle of maximum work, 308.
  of Soret, 208.
Properties of cathode rays, 33.
  of gels, 262.
Proportions, law of combining, 5.
  law of definite, 4.
  law of multiple, 5.
Protective colloids, 258.
Prout's hypothesis, 20.

Quantum Theory, 164.

Radiant energy, 504.
  source of, 505.
Radiations, nature of, 46.
  phosphorescence induced by, 46.
  photographic action of, 45.
Radioactive constant, 50.
  equilibrium, 52.
  substances, 44.
Radioactivity, 42.
  discovery of, 42.
Radio-elements, periodicity of, 61.
Radio-luminescence, 512.
Radium, 43.
  discovery of, 43.
  energy evolved by, 56.
Rays, α-, β-, and γ-, 47.
Ratio of charge to mass, 38.
  of specific heats, 96.

Ratio of charge to mass, of specific heats, determination of, 97, 98.
Reaction, determination of order of, 374.
  influence of solvent on velocity of, 378.
  velocity, 359, 374, 377.
Reactions, at constant pressure, 298.
  at constant volume, 298.
  bimolecular, 366.
  counter, 374.
  heterogeneous, velocity of, 376.
  of first order, 364.
  of higher orders, 373.
  of second order, 366.
  of third order, 370.
  photochemical, classification of, 519.
  side, 374.
  trimolecular, 370.
Reciprocal precipitation, 260.
Refraction, index of, 124.
  molecular, 126.
  specific, 126.
Residual current, 495.
Resistance capacity, 401.
Reversible cells, 448.
Rotation, magnetic, 139.
  molecular, 131.
  of plane polarized light, 129.
  specific, 131.

Salt solutions, thermoneutrality of, 305.
Saturated solution, 181.
Semi-permeable membranes, 187.
Side reactions, 374.
Solation, 239.
Solids, general properties of, 153.
  heat capacity of, 161.
Solubility coefficient, 171.
  product, 433.
Solutes, abnormal, 225.
Solution, association in, 225.
  dissociation in, 226.
Solution, heat of, 295.
  methods, 276.
  pressure, 450.
Solutions, 167.
  absorption in, 269.
  classification of, 167.
  colloidal, 238.
  conductance of non-aqueous, 418.
  imbibition in, 267.
  of gases in gases, 167.
  of gases in liquids, 167.
  of liquids in liquids, 172.
  of solids in liquids, 181.
  isohydric, 428.
  labile, 183.
  metastable, 183.
  properties of ionized, 231.
  saturated, 169.
  solid, 184.
  supersaturated, 169.
  volume-normal, 196.
  weight-normal, 196.
Solvate theory, 234.
Solvent, ionizing power of, 419.
Specific heat, 92, 93.
  and atomic weight, 11.
  at constant pressure and volume, 93.
  of gases, 100.
  of solid elements, 11, 161.
  ratio of, 96.
Specific refraction, 126.
  rotation, 131.
Spectra, absorption, 139.
Standard cells, 457.
Steam distillation, 179.
Strength of acids and bases, 424.
Sublimation, 153.
Submicrons, 239.
Sulphur, equilibrium between the phases of, 343.
Surface concentration, 272.
Surface energy of colloids, 271.
Surface tension, 144, 146, 149.
  of colloidal solutions, 247.

Suspensions, 239.
Suspensoids, 239.
  precipitation of, 254.
Systems, three-component, 356.
  two-component, 345.

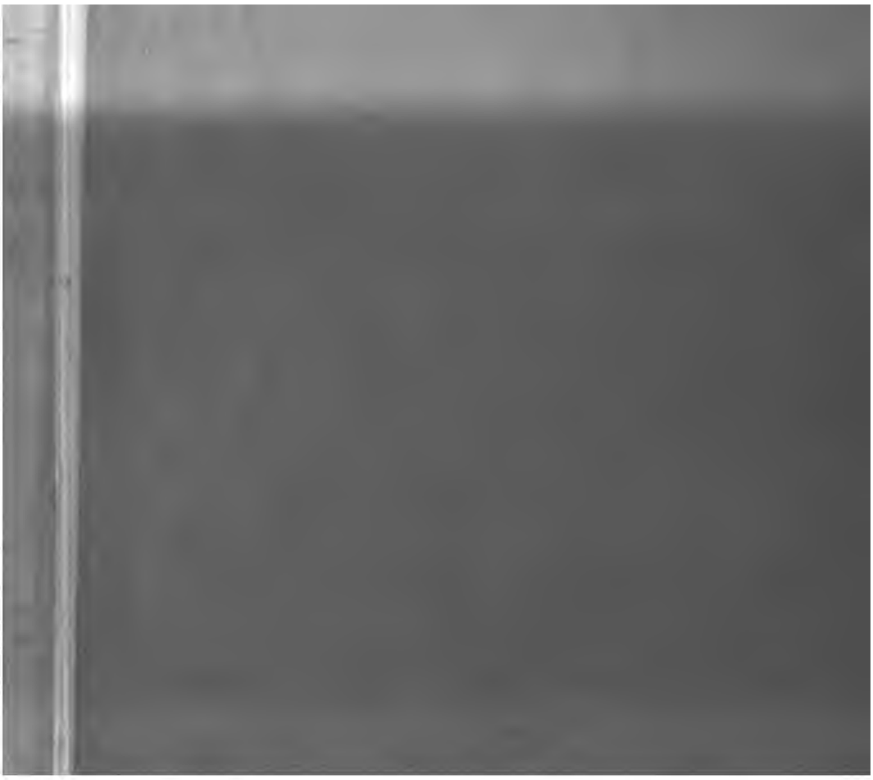
Theorem of Le Chatelier, 309.
Theory, electron, 31.
  kinetic, 100.
  of electrolytic dissociation, 227, 229.
  of solvation, 234.
Thermal units, 286.
Thermochemical equations, 287.
  measurements, 288.
Thermo-luminescence, 512.
Thermoneutrality of salt solutions, 304.
Transition point, 340.
Transmission coefficient, 514.
Transport numbers, 395.
  determination of, 395.
  electrometric determination of, 477.
Triads, of Döbereiner, 21.
Tribo-luminescence, 512.
Trimolecular reactions, 370.
Triple point, 342.
Tyndall phenomenon, 241.

Ultrafiltration, 242.
Ultramicroscope, 241.
Unimolecular reactions, 361, 364.
Units, electrical, 388.

Valence, 15.
  electrometric determination of, 476.
Vapor density, 83.
  abnormal, 88.
  determinations of, 86.
Vaporization, heat of, 118.
Vapor pressure, 117.
  and osmotic pressure, connection between, 211.
  lowering of, 209.
  of liquids, 117.
Variation of equilibrium constant with temperature, 337.
  of heat of reaction with temperature, 300.
Velocity constant, 315.
  of gaseous molecule, 80.
  of imbibition, 266.
Vibration, curves of molecular, 142.
Viscosity of colloidal solutions, 246.
Voltaic pile, 385.
Volume, molar, 10.
Volumes, Gay-Lussac's law of, 8.

Water, dissociation of, 414.
  equilibrium between phases of, 340.
  ionization constant of, 443.
  primary decomposition of, 501.
Weight, atomic, 8, 10, 17, 18.
  combining, 5, 8.
  gram-molecular, 10, 17.
  molar, 10, 17.

X-rays and atomic structure, 58.
  and crystal structure, 159.
  spectra, 60.



[illegible]